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Multiple Scattering Green-Function Method for Space-Filling Cell Potentials

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Abstract

It is shown that the equations of multiple scattering theory (MST) originally derived for scattering off collections of muffin-tin (MT) potentials, i.e., potential cells bounded by nonoverlapping spheres, remain valid in the case of arbitrarily shaped, nonoverlapping, and particularly space-filling potential cells. Specifically, it is shown that in the angular momentum representation the total scattering (transition) matrix, the Green function, the Bloch function for a translationally invariant material and the Lloyd formula for the change in the integrated density of states have forms that are invariant with respect to the partition of a given potential into nonoverlapping cells, and with respect to the choice of the cell centers. An analytic proof is provided for the vanishing of near-field-corrections (NFCs) long conjectured to arise when the spheres bounding individual cells overlap one another or adjacent potentials. Thus, the well-known MST expressions, originally derived for the case of MT potentials, for obtaining the solution of the Schrödinger equation and hence determining the bandstructure and the charge density of materials, ordered or disordered, are rigorously valid in the completely general case of arbitrarily shaped cells. The differences between this work and previous attempts to generalize MST to non-MT space-filling potentials are discussed. It is pointed out that in calculations involving non-MT potential cells, particular attention must be paid to the question of convergence of expansions in angular momentum eigenstates. This convergence is tested numerically in terms of cluster calculations and through the calculation of the electronic structure of elemental bcc Nb, and fcc Zr and Rh. The results of the cluster calculations confirm the vanishing of NFCs in the cases studied, while the electronic structure calculations indicate the rather rapid convergence that can be expected in applications of MST to close packed structures. The conclusions that can be drawn from the analytic and computational aspects of the present work are summarized in a final section, along with our plans for future work.

I. Introduction

At least formally, multiple scattering theory[1–6] (MST) provides a particularly transparent approach to the study of the electronic structure of matter and of related properties. Computationally the most useful form of MST is obtained in the angular momentum representation and in this form it has been widely applied in connection with potentials of the muffin-tin (MT) type, i.e., potential cells bounded by spheres that do not overlap one another or adjacent cells. Present day applications of MST are almost exclusively confined to MT potentials, based on the work of Korringa[4] and of Kohn and Rostoker[5] (KKR). Such applications have led to accurate determinations of the electronic structure of a large number of materials, especially metals[7] and substitutionally disordered metallic alloys.[8,9]

It can be said quite generally that MST occupies a unique position among all other methods that have been proposed for the calculation of electronic structure, for two principal reasons. First, it is in principle exact allowing within a single-particle picture the solution of the Schrödinger equation for complex materials with the proper boundary conditions taken into account. Thus, it treats in a unified manner a number of diverse physical systems that include, but are not limited to, pure, translationally invariant three-dimensional materials,[7] materials containing substitutional[8,9] or interstitial[10] impurities, displaced atoms,[11,12] and surfaces[13,14] and interfaces.[15] Second, it can lead directly to the calculation of the Green function from which all single-particle properties of a system can be obtained.

However, the formal integrity and practical usefulness of MST have been seriously compromised ever since the inception of the theory because of a vexing and all pervasive doubt. Namely, that MST can be used only in connection with MT potentials. It has been conjectured,[6,16–24] that in cases not satisfying the MT condition, one would have to take account of the so-called near-field-corrections (NFCs), which arise when the scattering of an outgoing spherical wave off a given potential cell begins before the scattering off the cell in which the wave originated has been completed. Mathematically, the difficulties can be associated with certain expansions of the free-particle propagator about shifted centers which, unless properly interpreted, can lead to divergent results. Given that the overlap between bounding spheres changes with different choices of the cell centers, i.e., the introduction of a shifted coordinate system, and also when a given potential is partitioned differently into cells, the presence of NFCs would render MST a rather unsatisfactory theory at a conceptual level. It would imply that certainly the form and possibly the results obtained in applications of MST would depend on representation (angular momentum, coordinate, partition into cells), and on the choice of a specific coordinate system. Given further that a large number of physically important problems, e.g., surfaces, impurities, alloys, etc., may require an accurate treatment of the potential throughout a unit cell, the need to calculate NFCs, an ill defined concept at best, would decrease substantially the applicability of MST making it of little, if any, use in the study of realistic physical problems. Fortunately, neither conceptually nor computationally is this the case.

It is the principal goal of the work presented in this paper to eliminate completely the doubt associated with MST. It will be shown that MST can be applied *intact to all* cases of non-MT, space-filling potentials of arbitrary, even interpenetrating shapes, and that in particular NFCs vanish identically. In fact, *all* results known from the application of MST to MT potentials hold rigorously in the case of generally shaped potentials with the only, inessential difference being the possible alternative methods of derivations or of different interpretations of certain expressions. Thus, MST will emerge as a proper physical theory not needful of modifications or corrections to its well-known MT form. In fact, *any* other method[6, 16–24] inequivalent to this form of MST is either approximate or fundamentally incorrect, failing to satisfy the basic properties of a proper physical theory mentioned above, i.e., independence of representation and of the choice of a coordinate system.

Our proof of the vanishing of NFCs brings forth the importance of the full scattering matrix of an assembly of scatterers as a criterion for measuring the effects of NFCs and in establishing their non-existence. Furthermore, it delineates these effects from those that may arise because of the lack of convergence in the expansions based on angular momentum eigenstates. Specifically, it is shown that the full scattering matrix of an assembly, and consequently the associated single-particle Green function, are invariant with respect to the partition of a given potential into cells and of the choice of the cell centers (centers of angular momentum expansions), retaining always the familiar MT form. This invariance, of course, exists in abstract operator space and in the coordinate, $\{\mathbf{r}\}$, representation, and here it is shown to exist in the computationally convenient angular momentum (L) representation as well. In fact, *all* algebraic manipulations of MST in operator space have exact analogues in the L representation. In addition to these formal considerations, we show explicitly the validity of the MT expressions for the Green function for any assembly of non-MT scatterers, for the Bloch function of translationally invariant materials, and for the Lloyd formula[25] for the change in the integrated density of states. The vanishing of NFCs is illustrated directly by means of cluster calculations. Also, the feasibility of using MST in calculating the electronic structure of materials described by non-MT space-filling potentials, at least for close packed lattices, is exemplified through calculations for elemental bcc Nb, and fcc Zr and Rh.

The remainder of the paper takes the following form: in Section II, we present a number of formal concepts, including a derivation of the fundamental equations of multiple scattering theory. We also point out the problems that may arise in certain non-MT cases and review a number of recent works concerned with the alleviation of these problems and the extension of MST to space-filling potentials. In this section we also discuss a number of criteria, including the empty lattice test, against which the validity of various forms of MST can be judged. Our formalism of MST for generally shaped potential cells, and the proof of the vanishing of NFCs are presented in Section III. In Section IV we derive the expressions for the single-particle Green function associated with any assembly of scatterers, and for the Bloch function and the Lloyd formula for materials with translational invariance. Section V contains the results of numerical calculations. Certain of these results indicate the integrity of the mathematical analysis employed in the proof of the vanishing of NFCs, while others verify directly that NFCs are zero in specific cases. The results of bandstructure calculations for elemental bcc NB, and fcc Zr and Rh illustrate the rather rapid convergence of the L expansions, at least in the case of materials with close-packed crystal structures. A discussion of our work, and the conclusions that can be drawn from it are collected in Section VI. Finally, a number of fundamental mathematical concepts, including the expansion properties of products of Bessel and Hankel functions with spherical harmonics, are given in Appendix A. Since the material presented in this appendix is basic to the formalism in the text, the reader may wish to consult this material before reading further.

II. Review of Underlying Concepts and of Former Work

A. Summary of Formal Scattering Theory

We present a brief overview of formal scattering theory, following by and large the presentation of Gell-Mann and Goldberger.[26] This overview is then used in the following subsection to derive the equations of MST, and to examine a number of previous attempts to extend MST to space-filling potentials. As is customary, we assume that the Hamiltonian, H_0, for a non-interacting system has only a continuous spectrum, while the Hamiltonian, $H = H_0 + V$, for the physical (interacting) system has the same continuous spectrum but may possess a discrete spectrum of bound states below the continuum. Thus, it is assumed that V does not support bound states in the continuous part of the spectrum. More detailed discussions of these and other commonly made assumptions of scattering theory may be found in the literature.[26-30]

1. Single-Potential Scattering

Given a Hamiltonian, H_0, with eigenstates[31] $|\chi_\alpha\rangle$,

$$H_0|\chi_\alpha\rangle = E_\alpha|\chi_\alpha\rangle \tag{2.1}$$

for a non-perturbed system, the scattered-wave solutions, $|\psi_\alpha^\pm\rangle$, of a perturbed system with Hamiltonian $H = H_0 + V$,

$$H|\psi_\alpha^\pm(V)\rangle = E_\alpha|\psi_\alpha^\pm(V)\rangle \quad , \tag{2.2.}$$

can be obtained by means of the Lippmann-Schwinger equations

$$|\psi_\alpha^\pm(V)\rangle = |\chi_\alpha\rangle + (E - H_0 \pm i\varepsilon)^{-1} V|\psi_\alpha^\pm(V)\rangle \quad , \tag{2.3}$$

where ε is a positive infinitesimal. The scattered-out, $|\psi_\alpha^+\rangle$, (scattered-in $|\psi_\alpha^-\rangle$) states are those that in the remote past (future) coincide with the free-particle state $|\chi_\alpha\rangle$, and correspond to the same eigenvalue, E_α. Although $|\psi_\alpha^-\rangle$ cannot be observed experimentally, i.e., one cannot prepare an interacting state in the infinite past that under the influence of the interaction V evolves into a free-state, its formal significance is indispensable in the development of scattering theory.[26] Introducing the Green functions at energy E,

$$G_0^\pm(E) = (E - H_0 \pm i\varepsilon)^{-1} \tag{2.4a}$$

and

$$G^\pm(E) = (E - H \pm i\varepsilon)^{-1} \tag{2.4b}$$

associated with the Hamiltonians H_0 and H, respectively, we can write Eq. (2.3) in a variety of equivalent forms. In the following, we consider explicitly only the case of outgoing waves and consequently drop the superscripts (±). (Incoming waves can be treated along similar lines.) Quite readily one obtains the expressions,[26,27]

$$\begin{aligned}|\psi_\alpha(V)\rangle &= |\chi_\alpha\rangle + G_0(E)\,V\,|\psi_\alpha(V)\rangle \\ &= |\chi_\alpha\rangle + G(E)\,V\,|\chi_\alpha\rangle \\ &= |\chi_\alpha\rangle + G_0(E)\,T(V)|\chi_\alpha\rangle \quad ,\end{aligned} \tag{2.5}$$

where the transition matrix (t-matrix, also somewhat loosely called the scattering matrix)

T(V) which is also a function of the energy parameter, E, is defined by the expression (with the energy arguments suppressed),

$$T(V) = V + V G_0 V + V G_0 V G_0 V + \dots \quad . \tag{2.6}$$

In discussions of scattering theory it is often assumed that this expansion converges and we shall follow this practice. Clearly, the quantity T(V) satisfies the Dyson equation

$$T(V) = V + V G_0 T(V) \quad , \tag{2.7}$$

which has the formal solution

$$\begin{aligned} T(V) &= \left(1 - V G_0\right)^{-1} V \\ &= \left(V^{-1} - G_0\right)^{-1} \quad . \end{aligned} \tag{2.8}$$

It follows from Eq. (2.5) that V and T(V) satisfy the relation

$$V\,|\psi_\alpha(V)\rangle = T(V)\,|\chi_\alpha\rangle \quad . \tag{2.9}$$

We note that the Lippmann-Schwinger equations can also be expressed in terms of the Green functions

$$\begin{aligned} G &= G_0 + G_0 V G \\ &= G_0 + G_0 T(V) G_0 \quad , \end{aligned} \tag{2.10}$$

which leads to the Green-function analogue of the wavefunction Eq. (2.9)

$$V G = T(V) G_0 \quad . \tag{2.11}$$

2. Two-Potential Scattering

Under the influence of two potentials, V + U, acting simultaneously, e.g., nuclear and Coulomb forces, the Lippmann-Schwinger equations have immediate and straightforward generalizations. Thus, we have for the wavefunction

$$\begin{aligned} |\psi_\alpha(V + U)\rangle &= |\chi_\alpha\rangle + G_0[V + U]|\psi_\alpha(V + U)\rangle \\ &= |\chi_\alpha\rangle + G_0T(V + U)|\chi_\alpha\rangle \quad , \end{aligned} \tag{2.12}$$

while for the Green function we obtain,

$$\begin{aligned} G &= G_0 + G_0[V + U]G \\ &= G_0 + G_0T(V + U)G_0 \quad . \end{aligned} \tag{2.13}$$

Equivalently, we can also write,

$$\begin{aligned} |\psi_\alpha(V + U)\rangle &= |\psi_\alpha(V)\rangle + G(V)\,U\,|\psi_\alpha(V + U)\rangle \\ &= |\psi_\alpha(V)\rangle + G(V)\,T(U/V)\,|\psi_\alpha(V)\rangle \end{aligned} \tag{2.14}$$

and

$$\begin{aligned} G &= G(V) + G(V)\,U\,G \\ &= G(V) + G(V)\,T(U/V)\,G(V) \end{aligned} \tag{2.15}$$

where $|\psi^\alpha(V)\rangle$ and G(V) are the wavefunction and Green function, respectively, associated with V alone, and T(U/V) denotes the scattering produced by U in a wave already distorted by V. This quantity provides the proper description of the scattering by U in the field of V. In recent attempts to generalize MST to space-filling potentials one encounters[23] a description of the scattering of a potential in a field which has not been shown to be equivalent to T(U/V). Such formulations not only are inconsistent with scattering theory, as they find no expression in operator space, but can be shown to lead to nonunique and hence nonphysical results.

Upon using Eq. (2.7) with respect to potentials V and V + U and properly combining terms we obtain the following relation

$$T(V + U) = T(V) + [1 + T(V)G_0]U[1 + G_0T(V + U)] \quad . \tag{2.16}$$

This equation can be used to derive the fundamental equations of MST, as is shown in the following subsection.

B. The Equations of Multiple Scattering Theory

Straightforward iteration of Eq. (2.16) yields the series

$$T(U + V) = T(V) + T(U) + T(V)\,G_0\,T(U) + T(U)\,G_0\,T(V)$$
$$+ T(V)\,G_0\,T(U)\,G_0\,T(V) + \dots \quad ,$$

where T(U) is the t-matrix, Eq. (2.8), corresponding to potential U acting alone. This equation has an immediate generalization in the case in which a number of potentials, V^i, with associated scattering matrices (t-matrices) $t(V^i) \equiv t^i$ act simultaneously. With

$$T \equiv T\left(\sum_{ij} V^i\right)$$

we readily find

$$T \equiv \left[\left(\sum_i V^i\right)^{-1} - G_0\right]^{-1} = \sum_{ij} T^{ij} \quad , \tag{2.17}$$

where the T^{ij} satisfy the so-called equation of motion

$$T^{ij} = t^i\delta_{ij} + t^i\,G_0\sum_{k\neq i} T^{kj} \quad . \tag{2.18}$$

Equations (2.17) and (2.18) constitute a set of fundamental equations of MST and are equivalent to those arrived at through alternative formulations.[6,27] Furthermore, Eq. (2.17) exhibits a fundamental property of T; the total scattering matrix depends only on the *total* potential, $\sum_i V^i$, and is entirely independent of the shape of the individual potential cells or of their extent. In the case of spatially bounded (finite extent) nonoverlapping potentials, certain important simplifications become possible. Introducing the free-particle propagator, G_0^{ik}, between potential cells i and k we can write Eq. (2.18) in the form,

$$T^{ij} = t^i \delta_{ij} + t^i \sum_{k \neq i} G^{ik} T^{kj} \quad . \tag{2.19}$$

Thus, T^{ij} can be obtained as the inverse of the matrix

$$M^{ij} = m^i \delta_{ij} - G_0^{ij}(1 - \delta_{ij}) \quad , \tag{2.20}$$

where $m^i \equiv (t^i)^{-1}$.

It is clear that the matrix elements T^{ij} and the associated Green-function matrix elements G^{ij} depend on the particular partition of a potential into cells and on the choice of the cell centers. On the other hand, as mentioned above, the full scattering matrix, T, and the associated full Green function are properly invariant with respect to such partitions and the choice of coordinates. As will be shown in a following section, this invariance is preserved when MST is expressed in the angular momentum representation.

For comparison with expressions to be derived later, we note that Eq. (2.17) can also be written in the form,

$$V = \sum_i V^i = \sum_i \left[T(V^i)^{-1} + G_0 \right]^{-1} \quad . \tag{2.17a}$$

Because the sum over cells equals the potential, V, Eq. (2.17a) clearly exhibits the invariance property of MST with respect to partition of V into cells.

C. Representations

1. The Coordinate Representation

In the coordinate representation, the abstract equations of scattering theory can be expressed as integral equations of the Fredholm type. With the usual notation $\psi(\mathbf{r}) = \langle \mathbf{r}|\psi\rangle$ and $G(\mathbf{r},\mathbf{r}') = \langle \mathbf{r}|G|\mathbf{r}'\rangle$, and for the case of local potentials we obtain the following expressions

$$\psi(\mathbf{r}) = \chi(\mathbf{r}) + \int G_0(\mathbf{r},\mathbf{r}')\, V(\mathbf{r}')\psi(\mathbf{r}')\, d^3r' \quad , \tag{2.3a}$$

$$\psi(\mathbf{r}) = \chi(\mathbf{r}) + \int G_0(\mathbf{r},\mathbf{r}')\, T(\mathbf{r}',\mathbf{r}'')\chi(\mathbf{r}'') d^3r'\, d^3r'' \quad , \tag{2.5a}$$

and

$$T(\mathbf{r},\mathbf{r}') = V(\mathbf{r})\left[\delta(\mathbf{r} - \mathbf{r}') + \int G_0(\mathbf{r},\mathbf{r}'')\, T(\mathbf{r}'',\mathbf{r}') d^3r''\right] \quad , \tag{2.7a}$$

corresponding to Eqs. (2.3), (2.5) and (2.7). Similar expressions can be obtained for the Green functions, e.g.,

$$\begin{aligned} G(\mathbf{r},\mathbf{r}') &= G_0(\mathbf{r},\mathbf{r}') + \int G_0(\mathbf{r},\mathbf{r}'')\, V(\mathbf{r}'') G(\mathbf{r}'',\mathbf{r}') d^3r'' \\ &= G_0(\mathbf{r},\mathbf{r}') + \int G_0(\mathbf{r},\mathbf{r}_1)\, T(\mathbf{r}_1,\mathbf{r}_2)\, G_0(\mathbf{r}_2,\mathbf{r}') d^3r_1\, d^3r_2 \quad . \end{aligned} \tag{2.10a}$$

It follows from Eq. (2.7a) that $T(\mathbf{r},\mathbf{r}')$ is identically zero when either $\mathbf{r}$ or $\mathbf{r}'$ is outside the potential region. In the usual applications of scattering theory, one is interested in the outgoing solutions of these equations corresponding to the use of G_0 which is given explicitly by the expression (in units of $\hbar^2/2m = 1$),

$$\begin{aligned} G_0(\mathbf{r},\mathbf{r}') &= -\frac{1}{4\pi}\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|} \\ &= G_0(\mathbf{r} - \mathbf{r}') \quad . \end{aligned} \tag{2.21}$$

It is convenient to identify cell-diagonal (cell-off-diagonal) elements of $G_0(\mathbf{r} - \mathbf{r}')$ according as to whether the arguments $\mathbf{r}$ and $\mathbf{r}'$ lie inside the same cell (different cells). It is also convenient to consider any two adjacent potential cells as being separated by a thin strip of zero potential whose contribution to the total scattering matrix, T, vanishes when its width is allowed to go to zero at the conclusion of formal considerations. We can now obtain the coordinate representation of the MST equation of motion, Eq. (2.19)

$$T^{ij}(\mathbf{r},\mathbf{r}') = t^i(\mathbf{r},\mathbf{r}')\delta_{ij} + \sum_{k\neq i}\int t^i(\mathbf{r},\mathbf{r}_1)\, G_0^{ik}(\mathbf{r}_1 - \mathbf{r}_2)\, T^{kj}(\mathbf{r}_2,\mathbf{r}')\, d^3r_1\, d^3r_2 \quad . \tag{2.22}$$

Here, $G^{ik}(\mathbf{r} - \mathbf{r}')$ is that cell-off-diagonal element of the free-particle propagator that corresponds to the vectors $\mathbf{r}$ and $\mathbf{r}'$ being confined to cells i and k, respectively. A similar interpretation holds for $T^{ij}(\mathbf{r},\mathbf{r}')$, although the scattering matrix is obviously not restricted to being off-diagonal in the site indices.

The essence of MST is readily discernable upon iteration of Eq. (2.22). This reveals the make up of the total scattering matrix as the sum of multiple scattering events off individual cells, described by the cell scattering matrices, $t^i(\mathbf{r},\mathbf{r}')$, with free propagation via $G_0^{ik}(\mathbf{r} - \mathbf{r}')$ between cells.

2. The Angular Momentum Representation

Informative as they may be, the integral equations of MST in the coordinate representation are very difficult to handle computationally. Under rather broad conditions, however, these equations can be transformed into equations in terms of matrices whose elements are indexed by L (= ℓ,m). In the angular momentum representation the total scattering matrix takes the form

$$T_{LL'} = \iint J_L(-\mathbf{r})\, T(\mathbf{r},\mathbf{r}')\, J_{L'}(\mathbf{r}')\, d^3r\, d^3r' \quad , \tag{2.23}$$

where $J_L(\mathbf{r}')$ denotes the spherical function $j_\ell(kr)\, Y_L(\hat{\mathbf{r}})$ defined in Appendix A. Using the vector/matrix notation introduced in Appendix A, we can write Eq. (2.23) in the form

$$\underset{\sim}{T} = \iint |J(-\mathbf{r})\rangle\, T(\mathbf{r},\mathbf{r}')\,\langle J(\mathbf{r}')|\, d^3r\, d^3r' \quad , \tag{2.24}$$

with undertildes denoting matrices in angular momentum space. Breaking the region of integration into integrations over the interiors of individual cells, and using the expansion properties of the functions $J_L(\mathbf{r})$, Eq. (A.4), we can write Eq. (2.24) in the form

$$\begin{aligned} \underset{\sim}{T} &= \sum_{i,j} \underset{\sim}{g}(-\mathbf{R}_i)\underset{\sim}{T}^{ij}\underset{\sim}{g}(\mathbf{R}_j) \\ &= \langle \underset{\sim}{g}\,|\underset{\approx}{T}|\,\underset{\sim}{g}^{\dagger}\rangle \quad . \end{aligned} \tag{2.25}$$

Here, $\underset{\sim}{T}^{ij}$ is given by the expression

$$\underset{\sim}{T}^{ij} = \int_{\Omega_i}\int_{\Omega_j} J_L(-\boldsymbol{\rho})\, T^{ij}(\boldsymbol{\rho},\boldsymbol{\rho}')\, J_L(\boldsymbol{\rho}')\, d^3\rho\, d^3\rho' \quad , \tag{2.26}$$

in which the integrals are confined to cells i and j, and $\boldsymbol{\rho}$ and $\boldsymbol{\rho}'$ are measured with respect to the centers of cells i and j, respectively, which are denoted by $\mathbf{R}_i$ and $\mathbf{R}_j$. In Eq. (2.25) we have also introduced the row (column) vectors $\langle \underset{\sim}{g}\,|(\,|\underset{\sim}{g}^{\dagger}\rangle)$ whose elements are the matrices $\underset{\sim}{g}(-\mathbf{R}_i) \equiv \underset{\sim}{g}_i \left[\underset{\sim}{g}^{\dagger}(\mathbf{R}_j) \equiv \underset{\sim}{g}^{\dagger}_j\right]$ and have used double undertildes to denote matrices in site and L space. We note that Eq. (2.25) is completely general, being valid for any set of scattering potentials regardless of their shape or the choices of the cell centers.

In general the operator T can have matrix elements between states with different energies, $\langle \chi_\alpha | T(V) | \chi_\beta \rangle = \langle \chi_\alpha | V | \psi_\beta \rangle$, with $E_\alpha \neq E_\beta$. In the ensuing discussion, and in general two-particle potential scattering theory, only the on-the-energy shell elements of T, $E_\alpha = E_\beta$, enter as is clear from the various integral expressions above. From now on the formalism will be developed in terms of these elements without a change in notation.

3. MT Potentials

Let us now specialize to the case of MT potentials. In this case the cell vectors $\boldsymbol{\rho}_i = \mathbf{r} - \mathbf{R}_i$ are confined inside nonoverlapping spheres and along with the vectors $\mathbf{R}_{ij} = \mathbf{R}_j - \mathbf{R}_i$ connecting the sphere centers satisfy the MT conditions, Eq. (A.18),

$$|\mathbf{R}_{ij} - \boldsymbol{\rho}_j| > |\boldsymbol{\rho}_i|, \qquad |\mathbf{R}_{ij} + \boldsymbol{\rho}_i| > |\boldsymbol{\rho}_j| \quad ,$$

and

$$|\mathbf{R}_{ij}| > |\boldsymbol{\rho}_i|, \qquad |\mathbf{R}_{ij}| > |\boldsymbol{\rho}_j|, \text{ and } |\mathbf{R}_{ij}| > |\boldsymbol{\rho}_i - \boldsymbol{\rho}_j| \quad .$$

Then the cell-off-diagonal element of the free-particle propagator, $G_0(\mathbf{r} - \mathbf{r}') \equiv G_0(\boldsymbol{\rho}_i + \mathbf{R}_{ij} - \boldsymbol{\rho}_j)$ can be expanded in terms of spherical functions, Eq. (A.19),

$$\begin{aligned} G_0(\boldsymbol{\rho}_i + \mathbf{R}_{ij} - \boldsymbol{\rho}_j) &= \sum_L H_L(\boldsymbol{\rho}_i + \mathbf{R}_{ij})\, J_L(\boldsymbol{\rho}_j) \\ &= \sum_{LL'} J_L(-\boldsymbol{\rho}_i)\, G_{LL'}(\mathbf{R}_{ij})\, J_{L'}(\boldsymbol{\rho}_j) \\ &= \langle J(-\boldsymbol{\rho}_i)|\, \underset{\sim}{G}(\mathbf{R}_{ij})\, |J(\boldsymbol{\rho}_j)\rangle \quad , \end{aligned} \tag{2.27}$$

where $\underset{\sim}{G}(\mathbf{R}_{ij})$ is a real space structure constant as defined in Eq. (A.10). Multiplying Eq. (2.22) from the left and from the right by $J_L(\mathbf{r})$ and $J_{L'}(-\mathbf{r}')$, respectively, and integrating, and using Eq. (2.27) and the definition, Eq. (2.24), we obtain the equation of motion in the matrix form,

$$\underset{\sim}{T}^{ij} = \underset{\sim}{t}^{i}\,\delta_{ij} + \underset{\sim}{t}^{i} \sum_{k \neq i} \underset{\sim}{G}^{ik}\, \underset{\sim}{T}^{kj} \quad , \tag{2.28}$$

where $\underset{\sim}{G}^{ik} = \underset{\sim}{G}(\mathbf{R}_{ik})$. It follows immediately from Eq. (2.28) that $\underset{\sim}{T}^{ij}$ is the (i,j)th matrix element of the inverse of a matrix $\underset{\approx}{M}$ whose elements are given by the expression

$$\underset{\sim}{M}^{ij} = \underset{\sim}{m}^{i}\delta_{ij} - \underset{\sim}{G}^{ij}(1 - \delta_{ij}) \quad . \tag{2.29}$$

We note that both Eqs. (2.28) and (2.29), obtained in the angular momentum representation, have identically the same form as the abstract operator Eqs. (2.19) and (2.20). In order to conform with established notation we shall henceforth denote the inverse of the matrix $\underset{\sim}{M}^{ij}$ by $\underset{\sim}{\tau}^{ij}$.

In the MT case, the quantity $\underset{\sim}{\tau}^{ij}$ is the on-the-energy shell scattering path operator[32] introduced by Györffy and Stott,[33] and in the form of Eq. (2.28) it is particularly convenient for computational purposes. This form clearly indicates the separation of the potential, embodied in the $\underset{\sim}{m}^{i}$, from the structural aspects of the system under study, which is reflected in the so-called real space structure constants (KKR structure constants), $\underset{\sim}{G}^{ij}$. Although for ease of computation the potentials inside the MT spheres are usually taken to be spherically symmetric, resulting in $\underset{\sim}{t}$ matrices that are diagonal in L, spherical symmetry is not formally necessary[34] for the validity of Eqs. (2.28) and (2.29). In the ensuing discussion, we shall refer to Eqs. (2.28) and (2.29) as the MT form.

At this point we will postpone a discussion of the forms taken in the MT case by various quantities, e.g., charge density or the single-particle Green function, the secular equation for the bandstructrue, and others, until we consider the general case of space-filling potentials in a later section. However, we wish to emphasize the fundamental significance of Eq. (2.28) and (2.29). The total scattering matrix for any assembly of MT scatterers can be obtained by means of Eq. (2.25) with $\underset{\sim}{\tau}^{ij}$ given by Eqs. (2.28) and (2.29). Thus, the solution of the Schrödinger equation for the *entire* potential has been obtained conveniently in terms of the solutions corresponding to individual cells, and quantities describing the structure of the material. It's worth noting that in the case of MT potentials the bandstructures obtained within the MST approach outlined above have been shown[35] to be formally identical to those obtained within the augmented plane wave method. The question now arises as to whether the MT form, Eqs. (2.28) and (2.29), can also be used to obtain the exact total scattering matrix in the case of arbitrarily shaped, non-MT potentials. The reasons for doubting the validity of these equations in the general case are set forth in the following subsection.

4. Non-MT Potentials and the Nature of the Problem

The passage from Eq. (2.22) to Eqs. (2.28) and (2.29), the MT form, made explicit use of the expansion of the free-particle propagator, Eq. (2.27). Strictly interpreted in terms of the summations indicated in its second line, Eq. (2.27) is valid only in the MT case. In this case, the summations over L and L′ can be performed independently of order and always lead[36] to converged results. Thus the MT conditions are sufficient for the validity of Eqs. (2.28) and (2.29). When the MT conditions are not satisfied, it is possible that the sums over L and L′ in Eq. (2.27) may become order dependent or even divergent, because the conditions ensuring the validity of Eq. (A.6) may not be satisfied. This situation may arise when the spheres bounding two adjacent cells overlap one another, or the potential in nearby cells. In this case it is not immediately evident that the quantity $\underset{\sim}{\tau}^{ij}$ obtained from Eq. (2.29) will lead to the correct total scattering matrix when used in Eq. (2.25). In fact, it has been conjectured[6,16–24,37] that in general the scattering path operator in the MT form *cannot* be used in the case of non-MT potentials, and that it must be modified to account for near-field corrections.

As we show in Section III, however, NFCs vanish identically, and in all cases the MT form, Eq. (2.29), provides the correct expression for $\underset{\sim}{\tau}^{ij}$, and for $\underset{\sim}{T}$ through Eq. (2.25). Before turning to that proof, we give in the next subsection a brief discussion of previous work associated with the applicability of MST to non-MT, space-filling potentials.

D. Previous Work

The original derivation of MST by KKR[4,5] was restricted to the case of MT potentials only. Kohn and Rostoker[5] suggested that the use of full cell t-matrices could not be justified because of possible divergences of certain L-expansions in the derivations, and that the potential outside the spheres inscribed in the cells could be treated by perturbation theory. This may have left the impression that the use of full cell t-matrices could be incorrect.

Matters stood somewhat dormant until 1974, when Williams and Van Morgan[16] (WM) suggested that the MT form of MST would be valid at least in certain cases, depending on the underlying structure. Not only is this suggestion correct, it reveals a relatively heightened sense of physical insight on the part of the authors. Their argument is essentially based on the principle that a representation cannot detract from the physical soundness of a theory, and in abstract operator space MST takes the MT form. Unfortunately, in attempting to derive their results, WM failed to provide a rigorous justification for the convergence of certain L summations in the expansions of G_0, and these expansions may in fact diverge. In addition, even if the summations *had* been justified, the resulting theory would still contain nonphysical characteristics because it would apply only to specific choices of cell partitions and cell centers.

The work of WM was attacked on the issue of convergence almost immediately upon its appearance. First Ziesche[20] and a few years later Faulkner[6] and other authors[19] pointed out the conceptual difficulties in the work of WM. Although the criticism is well taken, the conclusions based on it have been fundamentally wrong. Setting aside the purely mathematical aspects of the issue, we can consider the physical argument that has been proposed to justify the existence of NFCs. Namely, a spherical wave emanating from the center of a nonspherical cell, could begin scattering off an adjacent cell before the scattering off the original cell has been completed. It is then argued that the scatterings off the two cells must be inextricably coupled, rendering any description in terms of individual scattering matrices invalid.

This argument can be attacked and disposed off on general principle and in terms of computational examples. We may recall Huygen's principle stating that each point of an advancing wavefront acts independently as a source of secondary spherical waves whose interference determines the form of the wave at subsequent time intervals. With this we couple the fundamental character of multiple scattering expansions as probabilistic, i.e., that one may ignore scattering off given potential cells in setting up the scattering sequences as long as the *totality* of the terms includes all scatterers. Were this not true, even the scattering off MT cells would not be expressible in its well known form. A wave propagating from cell to cell would have to scatter off *all* intervening cells making the use of the scattering matrices of individual cells illegitimate. The resolution of these difficulties can be achieved on the basis of the following, consistent and contradiction-free description of wave scattering in the presence of arbitrary numbers of scatterers: Each point on any wave front scatters off the local potential in its vicinity, and it is the interference of all these secondary wavelets, each multiply scattered according to this same prescription, which finally determines the outgoing wave. The notion of multiply scattered wavelets was also interjected by Keister[37] who concluded that in certain cases NFCs must vanish. Keister's formalism became considerably involved in the case of interpenetrating potentials causing the author to advise caution in applying it.

But what is to be done with the apparent difficulty of reconciling correct physical principle with proper mathematical formalism? This question is settled in Section III, where it is shown that expanding *around* rather than *through* the pole of G_0 and considering any cell as a collection of spheres allows one to obtain converged expressions for the scattering matrix in the MT form.

On the computational front, Faulkner[6,38] has made a valiant effort to evaluate NFCs in the case of a square lattice with a constant potential (the empty lattice test). These numerical investigations have not yielded conclusive evidence supporting the existence of NFCs. Some of the eigenvalues of the secular equation converge properly to their correct values indicating clearly the absence of NFCs. The $L = 0$ eigenvalue appears to follow a $1/L$ rate, leaving in doubt the positions of the last two points on the graph. Thus, the 2.5% difference with the exact results which Faulkner[38] suggests may be attributed to NFCs, could in fact arise because of lack of convergence or numerical instability, or both. The fact that this difference is small is no consolation and does not justify the use of

Eq. (2.29) in the case of non-MT potentials. Because the origin of the difference is unclear, so would be its magnitude in a different case.

In attempting to avoid the difficulties of "near-field effects," Brown and Ciftan (BC)[17,23] arrived at a secular equation determining the bandstructure of a material composed of space-filling cells, which is of the MT form *but* with the role of the cell scattering matrices, $\underset{\sim}{t}^{i}$, being played by a quantity defined in a rather different way.

However, the authors have not shown that the use of this "cell scattering" quantity in the secular equation can produce the proper matching of the wavefunction across cell boundaries. As will be discussed in the following subsection, doubts about the formalism of BC can also be raised with regard to a number of criteria which a proper physical theory should satisfy.

A different secular equation has been proposed by Badralexe and Freeman (BF).[24] However, that secular equation amounts to no more than a restatement of the Schrödinger equation for the whole potential, with no effort being made to take advantage of the concepts in MST. Consequently, the resulting theory is computationally useless. It is also interesting to note that the secular equation proposed by BF reduces to that of KKR for the case of MT potentials, while in their most recent work these authors arrive at the conclusion that the KKR formalism is only approximate even for that case!

For somewhat different reasons, the original work of Zeller,[35] also fails to settle the issue of NFCs. The use of a convergence factor, as proposed in that work, addresses only the numerical aspects of the convergence problem, while the validity of the final expressions should be independent of such a factor. In addition, the presence of a convergence factor in the final expressions for $\underset{\sim}{M}^{ij}$ proposed by Zeller leads to results that depend on the choice of cell centers, thus compromising uniqueness, and can lead to incorrect results even in the MT case and last, but not least, render the corresponding expressions computationally cumbersome.

In more recent work,[39] Zeller has succeeded in obtaining an essentially analytic solution for the empty lattice test within a KKR formalism, under certain restrictions to the shape of the cells and the choice of the cell centers. In spite of these restrictions and the fact that the analysis presented by Zeller does not justify formally the use of Eq. (2.29) in the general non-MT case, this work provides a powerful counterexample to the conjecture of the existence of NFCs, and to any statements[24] disputing the validity of the MT form in the case of space-filling potentials. Under the same restrictions to the shape of the cells, Gonis[40] has shown analytically that NFCs vanish in the case of the two-scatterer problem, a result which has been extended to the case of arbitrary number of convex scatterers by Molenaar.[41]

Finally, using a generalization of the Wigner R-matrix formalism, Nesbett[42] has recently succeeded in separating the structure and the potential aspects of a bandstructure calculation also in the restricted non-MT case of convex cells. Thus, as matters stand at present, it can be said that the general existence of NFCs has been infused with great doubt, but a rigorous proof that NFCs vanish in all cases has not been given. Such a proof is provided in Section III.

In closing this section we note that *all* previous methods proposed for extending MST to non-MT potentials yield results that depend on the particular way a given potential is partitioned into cells and on the choice of cell centers. Thus, they fail to satisfy an important requirement of proper physical theory: that results must be independent of both the introduction of a particular representation (partition into cells) and of a particular coordinate system (choice of cell origins). This is indeed the case when MST is expressed in abstract operator space or in the coordinate representation, as we saw earlier. It remains the case when MST is expressed in the angular momentum representation.

E. Criteria of Proper Scattering Theory

Before proceeding with a rigorous proof of the validity of MST for generally shaped potentials, it may be instructive to cite a number of criteria that must be satisfied by a proper, physically meaningful theory of multiple scattering. Any reformulation of MST should be judged against these criteria before its validity can be ascertained.

a: The empty lattice test

In the empty lattice test one is required to use a particular form of MST to reproduce the known eigenvalues of a Hamiltonian associated with empty space with a shifted constant potential. In spite of the conceptual simplicity of this test, its only proper application to date has been made in terms of numerical studies.[38,39] As is well known, however, numerical studies can only disprove a theory, and can do so only if they reveal discrepancies with known exact results that are beyond reasonable doubt. In light of this, none of the previous numerical studies of the empty lattice test has disproved the validity of MST in its MT form.

b: The reproduction of exact terms in MST expansions.

Consider that series of terms in the MST expansions, see Eq. (2.22), for any multicell scattering assembly which involves two given scatterers so far apart that the MT formalism is valid (i.e., the spheres bounding the two scatterers do not overlap). Then in abstract operator space, in the coordinate representation, and in the angular momentum representation the scattering off this pair in the field of all other scatterers is obtained through the series,

$$t_1 \, G_{12} \, t_2 + t_2 \, G_{21} \, t_1 + t_1 \, G_{12} \, t_2 \, G_{21} \, t_1 + t_2 \, G_{21} \, t_1 \, G_{12} \, t_2 + \cdots \quad . \tag{2.30}$$

We suggest that *any* MST expansion should reproduce such exact terms, and that any failure to do so is sufficient grounds for its disqualification.

c Shifted centers.

Consider a given collection of scattering centers and choose the centers of the cells in two different ways. As this corresponds to a change in the origin of cell coordinates it should not affect the results of calculations of physical quantities. Any theory or form of

MST which can be shown to depend on such shifts can readily be disqualified as non-physical.

Let us now judge the forms proposed by Faulkner[6,38] (modified structure constants), by Brown and Ciftan[23] (modified single-cell scatterers) and the formalism of Badralexe and Freeman[24] (a restatement of the Schrödinger equation) against these criteria.

Faulkner's NFCs formulation passes test b by default, because the scatterers are far apart and NFCs are stipulated to vanish. It fails, however, test c even in the case of MT potentials. To see this consider two MT scatterers with their centers so chosen that the sphere bounding either cell overlaps the other scatterer. Now, in Faulkner's formulation the structure constant connecting the two centers is a function of potential. In general the eigenvalues of the scattering matrix will be different from those obtained from the matrix when the centers are chosen so that the bounding spheres do not overlap. Thus, the two matrices cannot be related by a unitary transformation, depending only on the shift of the cell centers, and one obtains the unphysical result that a shift in the origin of the cells results in different physical properties of the system. In terms of test a, no evidence of the existence of NFCs has been found in numerical studies as mentioned previously.

Regarding the work of BC, it can easily be seen that if their cell scattering matrices are different from those associated with isolated cells, and are dependent on the part of the surrounding potential covered by a bounding sphere, then their secular equation fails both tests b and c. Finally, the "proof" that this formalism satisfies test a, provided by Brown,[23] did not make use of the secular equation and is, therefore, irrelevant.

Badralexe and Freeman[24] have made strong claims about the validity of their "theory" on the grounds that it satisfies the empty lattice test. However, one should expect that this test be satisfied by any theory which simply restates the Schrödinger equation. Of course, the other tests are not possible because the formalism of BF is divorced from MST.

III. The Vanishing of Near-Field Corrections and Multiple Scattering Theory for Space-Filling Potentials

A. Preliminary Notions

There are at least two different approaches that one may take in attempting to study the problem of NFCs. One could either attempt to sum any troublesome expansions directly, or one could prove the validity of the MT form by independent means, bypassing the difficulties associated with the expansions in the t-matrices. As is indicated by a large and rather unsuccessful body of work,[6,16–34,37,38] the first approach is not a particularly fruitful one. Our proof of the vanishing of NFCs will be based on proving independently the validity of the MT form in obtaining the total scattering matrix, $\underset{\sim}{T}$, from $\underset{\sim}{t}^{ij}$.

As we pointed out in the last section, the scattering matrix, $\underset{\sim}{T}$, defined in Eq. (2.25), is invariant with respect to the partition of a given potential into cells and with respect to the choice of the cell centers. We will now show that the $\underset{\sim}{t}^{ij}$, given by Eq. (2.29) in the MT form, lead to the exact $\underset{\sim}{T}$ when used in Eq. (2.25) in all cases, regardless of the shape of the individual cells, or the positions of their centers. Because the proof of invariance with respect to cell centers is the simpler of the two tasks, we begin with that.

B. Invariance With Respect to Cell Centers

Consider an arbitrary number of generally shaped, nonoverlapping potentials and the associated matrix $\underset{\sim}{M}^{ij}$ written in the MT form. Choose a set of vectors $\{\mathbf{a}_i\}$ such that for any i and j the vectors $\mathbf{R}_j - \mathbf{R}_i$ satisfy the MT conditions, Eq. (A.18), with respect to the vectors $\mathbf{a}_i$ and $\mathbf{a}_j$ (in fact it is only necessary to consider $|\mathbf{R}_j - \mathbf{R}_i|$ greater than $|\mathbf{a}_i|$ and $|\mathbf{a}_j|$, along with $|\mathbf{R}_j - \mathbf{R}_i - \mathbf{a}_j| > |\mathbf{a}_i|$ and $|\mathbf{R}_j - \mathbf{R}_i + \mathbf{a}_i| > |\mathbf{a}_j|$), and apply a similarity transformation to $\underset{\sim}{M}^{ij}$ by means of the matrix

$$[\underset{\sim}{g}]_{ij} = \underset{\sim}{g}(\mathbf{a}_i)\,\delta_{ij} \quad . \tag{3.1}$$

Because of the MT conditions between the vectors $\mathbf{R}_i - \mathbf{R}_j$, and $\mathbf{a}_i$ and $\mathbf{a}_j$, we obtain

$$\hat{\underset{\sim}{M}}^{ij} = \underset{\sim}{g}(\mathbf{a}_i)\,\underset{\sim}{m}^i\,\underset{\sim}{g}^\dagger(\mathbf{a}_i)\,\delta_{ij} - \underset{\sim}{G}(\mathbf{R}_j - \mathbf{R}_i + \mathbf{a}_j - \mathbf{a}_i)(1 - \delta_{ij}) \quad , \tag{3.2}$$

for the transformed matrix. We note that $\hat{\underset{\sim}{M}}^{ij}$ is of the MT form corresponding to the cell center at $\mathbf{R}_i$ being shifted to $\mathbf{R}_i + \mathbf{a}_i$. This process of shifting the centers can be repeated indefinitely leading to an expression of the form of Eq. (3.2), the MT form, but with the final vectors $\mathbf{a}_i$ having arbitrary length. Clearly, the overlap between the bounding spheres can change arbitrarily as the centers of the spheres are shifted, and it may be expected that NFCs change correspondingly.

However, we can easily realize that the eigenvalues of $\underset{\approx}{M}$ remain invariant under the series of similarity transformations producing the shifted centers. Most importantly, $\hat{\underset{\approx}{M}}^{-1}$ and $\underset{\approx}{M}^{-1}$ yield identical results for $\underset{\sim}{T}$ when used in Eq. (2.25). To see this, we note that $\underset{\sim}{T}$ remains unchanged when the unit matrix in the form $\underset{\sim}{g}(\mathbf{a}_i)\,\underset{\sim}{g}^\dagger(\mathbf{a}_i)$ is inserted between the products of $g(\mathbf{R}_i)$ and $\underset{\sim}{\tau}^{ij}$ in Eq. (2.25) (see following subsection). Thus, $\underset{\sim}{T}$ is invariant under a shift of the cell origins implying that NFCs must also have the same property.

C. The Vanishing of Near-Field Corrections

The discussion just given shows that NFCs remain constant under a shift in the cell centers, but does not guarantee that they vanish. To prove this last assertion we must show that NFCs are also invariant with respect to the cell shape. The proof is based on the ansatz that any cell potential can be represented to any desired degree of accuracy by a collection of spherical cells. This can be accomplished through the introduction of the largest possible spheres in any as yet uncovered regions until the remaining uncovered region shrinks below a predetermined value. (Under this process, only sets of measure zero, which do not contribute to volume integrals or to the cell t-matrix can remain uncovered). The scattering matrix of the collection of such spheres, obtained through Eq. (2.25), which is valid for arbitrary numbers of cells, can be made arbitrarily close to the true scattering matrix of the cell as the number of spheres increases beyond all bounds. We will now show that NFCs *are the same when the cells are considered as collections of spheres, (MT potentials), as when they are considered as individual units.* Because by definition NFCs are equal to zero in the former case they must vanish identically in all cases. This will be shown to be true in the most general case of spatially bounded, nonoverlapping potentials including potentials with interpenetrating boundaries. A preliminary account of the following proof has been given in a previous publication.[43]

We consider a potential, V, partitioned arbitrarily into nonoverlapping cells with potentials V_i, $V = \sum_i V_i$, of arbitrary shape but with finite range. We interpret the last condition to imply the existence of radii r_i such that $V_i(\mathbf{r}) = 0$ for $|\,\mathbf{r}\,| \rangle r_i$. In the following proof we use the expansion property[43] of the coefficients $\underset{\sim}{G}(\mathbf{R})$, $\underset{\sim}{G}(\mathbf{R})\,\underset{\sim}{g}(\mathbf{a}) = \underset{\sim}{G}(\mathbf{R} - \mathbf{a})$ for $|\,\mathbf{R}\,| > |\,\mathbf{a}\,|$ [see also Eq. (A.15)], to obtain $\underset{\sim}{G}(\mathbf{R} - \mathbf{a})$ from $\underset{\sim}{G}(\mathbf{R})$ even for $|\,\mathbf{a}\,| \geq |\,\mathbf{R}\,|$. This can be done by expanding around the pole of $\underset{\sim}{G}(\mathbf{R})$ using an inherently convergent stepwise process in which $\mathbf{a}$ is broken into a sum,

$$\mathbf{a} = \sum_{\alpha=1}^{N} \mathbf{a}_\alpha , \qquad \text{such that } |\,\mathbf{R} - \sum_{\alpha=1}^{n} \mathbf{a}_\alpha\,| > |\,\mathbf{a}_{n+1}\,| \text{ for all } n \leq N \text{ as follows:}$$

$$\begin{aligned}
\underset{\sim}{G}(\mathbf{R} - \mathbf{a}) &\equiv \underset{\sim}{G}\left(\mathbf{R} - \sum_{\alpha=1}^{N} \mathbf{a}_\alpha\right) = \underset{\sim}{G}\left(\mathbf{R} - \sum_{\alpha=1}^{N-1} \mathbf{a}_\alpha\right) \underset{\sim}{g}(\mathbf{a}_N) \\
&= \ldots = \left\{\left[\underset{\sim}{G}(\mathbf{R})\, \underset{\sim}{g}(\mathbf{a}_1)\right] \underset{\sim}{g}(\mathbf{a}_2)\right\} \cdots \underset{\sim}{g}\,\mathbf{a}_N \\
&\equiv G(\mathbf{R}) \odot g(\mathbf{a}) \quad . \qquad (3.3)
\end{aligned}$$

(This process is not always possible in strictly one-dimensional geometries, but NFCs do not arise in one-dimension). We shall use the symbol $\odot$ to denote such a convergent process or matrix multiplication.

Now consider the total t-matrix, $\underset{\sim}{T}'$, obtained using the MT form, Eq. (2.29), for $\underset{\sim}{M}^{ij}$ with the $\underset{\sim}{m}^i = (\underset{\sim}{t}^i)^{-1}$ in that equation being the inverses of the individual cell scattering matrices. We will show that $\underset{\sim}{T}'$ is identical to the exact $\underset{\sim}{T}$. For arbitrary vectors **a** and **b** one can write

$$\underset{\sim}{T}' = \langle \underset{\sim}{g} \,|\, \underset{\sim}{g}(\mathbf{a})\underset{\sim}{g}^{\dagger}(\mathbf{a})\underset{\approx}{\tau}\underset{\sim}{g}(\mathbf{b})\underset{\sim}{g}^{\dagger}(\mathbf{b}) \,|\, \underset{\sim}{g}^{\dagger}\rangle = \underset{\sim}{g}(\mathbf{a})\langle \underset{\sim}{g} \,|\, \underset{\approx}{\tau}^{ab} \,|\, \underset{\sim}{g}^{\dagger}\rangle\underset{\sim}{g}^{\dagger}(\mathbf{b}) \quad , \tag{3.4}$$

where $\underset{\approx}{\tau}^{ab} = \underset{\sim}{g}^{\dagger}(\mathbf{a})\underset{\approx}{\tau}\underset{\sim}{g}(\mathbf{b})$ with $\underset{\approx}{\tau}$ given as the inverse of $\underset{\approx}{M}$ defined in Eq. (2.29). Using the process defined in Eq. (3.3) one obtains the result,

$$[(\underset{\approx}{\tau}^{ab})^{-1}]_{ij} = \underset{\sim}{g}^{\dagger}(\mathbf{b})\,\underset{\sim}{m}^{i}\,\underset{\sim}{g}(\mathbf{a})\,\delta_{ij} - \underset{\sim}{G}^{ab}_{ij}(1 - \delta_{ij}) \quad , \tag{3.5}$$

where $\underset{\sim}{G}^{ab}_{ij} \equiv \underset{\sim}{G}(\mathbf{R}_j - \mathbf{R}_i + \mathbf{b} - \mathbf{a})$.

At this point, we define the "full" free-particle propagator $[\bar{\underset{\approx}{G}}^{ab}]_{ij} \equiv \underset{\sim}{G}(\mathbf{b} - \mathbf{a})\,\delta_{ij} + \underset{\sim}{G}^{ab}_{ij}(1 - \delta_{ij})$. Upon choosing a sufficiently large vector $(\mathbf{b} - \mathbf{a})$, we can write $\bar{\underset{\approx}{G}}^{ab} = |\,\underset{\sim}{g}^{\dagger}\rangle\underset{\sim}{G}(\mathbf{b} - \mathbf{a})\langle \underset{\sim}{g}\,|$ and hence obtain the expression

$$\underset{\approx}{\tau}^{ab} = \left[\underset{\approx}{\eta}^{ab} - |\,\underset{\sim}{g}^{\dagger}\rangle\underset{\sim}{G}(\mathbf{b} - \mathbf{a})\langle \underset{\sim}{g}\,|\right]^{-1} \quad ,$$

where $[\underset{\approx}{\eta}^{ab}]_{ij} = \left[\underset{\sim}{g}^{\dagger}(\mathbf{b})\underset{\sim}{m}^{i}\underset{\sim}{g}(\mathbf{a}) + \underset{\sim}{G}(\mathbf{b} - \mathbf{a})\right]\delta_{ij}$. Multiplying $\underset{\approx}{\tau}^{ab}$ on the left (right) by $\langle \underset{\sim}{g}\,|$ $(|\,\underset{\sim}{g}^{\dagger}\rangle)$ we obtain

$$\langle \underset{\sim}{g} \,|\, \underset{\approx}{\tau}^{ab} \,|\, \underset{\sim}{g}^{\dagger}\rangle = \langle \underset{\sim}{g}\,|\left[\underset{\approx}{\eta}^{ab} - |\,\underset{\sim}{g}^{\dagger}\rangle\underset{\sim}{G}(\mathbf{b} - \mathbf{a})\langle \underset{\sim}{g}\,|\right]^{-1}|\,\underset{\sim}{g}^{\dagger}\rangle \quad . \tag{3.6}$$

Next, we define the matrices

$$[\underset{\approx}{G}]_{ij} = \underset{\sim}{G}(\mathbf{b} - \mathbf{a})\delta_{ij}$$

and

$$[\underset{\approx}{g}]_{ij} = \begin{cases} \underset{\sim}{g}_{oj} & i = 0 \\ \varepsilon\underset{\sim}{I}\,\delta_{ij} & i \neq 0, \end{cases}$$

where $\underset{\sim}{I}$ is the unit matrix and ε is an infinitesimal, so that the right-hand side of Eq. (3.6) can be expressed in the form,

$$\left\{\underset{\approx}{g}\left[\underset{\sim}{\eta}^{ab} - \underset{\approx}{g}^{\dagger}\underset{\approx}{G}\underset{\approx}{g}\right]^{-1}\underset{\approx}{g}^{\dagger}\right\}_{\infty} + 0(\varepsilon) = \left\{\left[\left[\underset{\approx}{g}(\underset{\sim}{\eta}^{ab})^{-1}\underset{\approx}{g}^{\dagger}\right]^{-1} - \underset{\approx}{G}\right]^{-1}\right\}_{\infty} + 0(\varepsilon) \tag{3.7}$$

where $0(\varepsilon)$ denotes terms of order ε and higher. Thus, in the limit $\varepsilon \rightarrow 0$, Eq. (3.6) becomes

$$\langle \underset{\sim}{g} \mid \underset{\sim}{\tau}^{ab} \mid \underset{\sim}{g}^{\dagger} \rangle = \left[\langle \underset{\sim}{g} \mid (\underset{\approx}{\eta}^{ab})^{-1} \mid \underset{\sim}{g}^{\dagger} \rangle^{-1} - \underset{\sim}{G}(\mathbf{b} - \mathbf{a})\right]^{-1} \quad . \tag{3.8}$$

Then, defining $\underset{\sim}{M}' \equiv \left(\underset{\sim}{T}'\right)^{-1}$, and inverting and combining Eqs. (3.4) and (3.8) we obtain the important result,

$$\begin{aligned}\left[\underset{\sim}{g}^{\dagger}(\mathbf{b})\underset{\sim}{M}'\underset{\sim}{g}(\mathbf{a}) + \underset{\sim}{G}(\mathbf{b} - \mathbf{a})\right]^{-1} &= \langle \underset{\sim}{g} \mid (\underset{\approx}{\eta}^{ab})^{-1} \mid \underset{\sim}{g}^{\dagger} \rangle \\ &= \sum_{i} \underset{\sim}{g}(\mathbf{R}_i)\left[\underset{\sim}{g}^{\dagger}(\mathbf{b})\underset{\sim}{m}^{i}\underset{\sim}{g}(\mathbf{a}) + \underset{\sim}{G}(\mathbf{b} - \mathbf{a})\right]^{-1}\underset{\sim}{g}^{\dagger}(\mathbf{R}_i) \quad .\end{aligned} \tag{3.9}$$

The matrix $\underset{\sim}{T}'$ obtained from Eq. (3.9) is identical to the exact total $\underset{\sim}{T}$ in the MT case, because Eq. (2.29) is exact in that case. We now show that $\underset{\sim}{T}'$ is identical to $\underset{\sim}{T}$ in all cases. To this end, we can represent any cell potential, V_i, to any desired accuracy by a collection of nonoverlapping MT potentials, $V_{i\alpha}$, centered at $\mathbf{R}_{i\alpha}$ relative to the cell center $\mathbf{R}_i$. Thus, we can express the inverse cell scattering matrix, $\underset{\sim}{m}^{i}$, in terms of the $\underset{\sim}{m}^{i\alpha}$, which correspond to the MT potentials, $V_{i\alpha}$. Using Eq. (3.9), which is exact in this case, we obtain

$$\left[\underset{\sim}{g}^{\dagger}(\mathbf{b})\underset{\sim}{m}^{i}\underset{\sim}{g}(\mathbf{a}) + \underset{\sim}{G}(\mathbf{b} - \mathbf{a})\right]^{-1} = \sum_{\alpha} \underset{\sim}{g}(\mathbf{R}_{i\alpha})\left[\underset{\sim}{g}^{\dagger}(\mathbf{b})\underset{\sim}{m}^{i\alpha}\underset{\sim}{g}(\mathbf{a}) + \underset{\sim}{G}(\mathbf{b} - \mathbf{a})\right]^{-1}\underset{\sim}{g}^{\dagger}(\mathbf{R}_{i\alpha}) \quad . \tag{3.10}$$

Finally, upon substituting Eq. (3.10) into Eq. (3.9) we obtain the result,

$$\begin{aligned}&\left[\underset{\sim}{g}^{\dagger}(\mathbf{b})\underset{\sim}{M}'\underset{\sim}{g}(\mathbf{a}) + \underset{\sim}{G}(\mathbf{b} - \mathbf{a})\right]^{-1} = \\ &\qquad \sum_{i,\alpha} \underset{\sim}{g}(\mathbf{R}_i)\underset{\sim}{g}(\mathbf{R}_{i\alpha})\left[\underset{\sim}{g}^{\dagger}(\mathbf{b})\underset{\sim}{m}^{i\alpha}\underset{\sim}{g}(\mathbf{a}) + \underset{\sim}{G}(\mathbf{b} - \mathbf{a})\right]^{-1}\underset{\sim}{g}^{\dagger}(\mathbf{R}_{i\alpha})\underset{\sim}{g}^{\dagger}(\mathbf{R}_i) \quad .\end{aligned} \tag{3.11}$$

Because the right-hand side of Eq. (3.11) can be viewed as a single sum over non-overlapping MT potentials, this equation yields a matrix $\underset{\sim}{T}'$, identical to the exact $\underset{\sim}{T}$, independently of the partition of V into cell potentials, V_i. In other words, *this is precisely the form for* $\underset{\sim}{M}'$ *that would have been obtained with the total potential, V, being viewed as a collection of the MT potentials,* $V_{i\alpha}$*, from the beginning.* It follows that near-field corrections must vanish identically in all cases.

The proof of the vanishing of NFCs has a number of important consequences. First, it shows that $\underset{\sim}{T}$ obtained from Eq. (2.25) with $\underset{\sim}{t}$ in the MT form is indeed the solution of the Schrödinger equation [more precisely of Eq. (2.7)], associated with the entire potential of a system. Second, it allows the performance of algebraic manipulations in angular momentum space, which are the direct analogues of those in abstract operator space, thus bringing forth the integrity of the former representation of MST. Note that with the quantities $\underset{\sim}{g}_i\left[\underset{\sim}{g}^\dagger(\mathbf{b})\underset{\sim}{m}^i\underset{\sim}{g}(\mathbf{a}) + \underset{\sim}{G}(\mathbf{b} - \mathbf{a})\right]^{-1}\underset{\sim}{g}_i^\dagger$ playing the role of V_i^{-1} in Eq. (2.17), and with $\underset{\sim}{G}(\mathbf{b} - \mathbf{a})$ playing the role of G_0, Eq. (3.9) written in the form

$$\underset{\sim}{T} = \underset{\sim}{g}(\mathbf{a})\left\{\left[\sum_i \underset{\sim}{g}(\mathbf{R}_i)\left[\underset{\sim}{g}^\dagger(\mathbf{b})\underset{\sim}{m}^i\underset{\sim}{g}(\mathbf{a}) + \underset{\sim}{G}(\mathbf{b} - \mathbf{a})\right]^{-1}\underset{\sim}{g}^\dagger(\mathbf{R}_i) - \underset{\sim}{G}(\mathbf{b} - \mathbf{a})\right]^{-1}\right\}\underset{\sim}{g}^\dagger(\mathbf{b}) \quad , \qquad (3.12)$$

is the precise analogue of Eq. (2.17). Third, the invariance of $\underset{\sim}{T}$ with respect to partition into cells and the choice of cell centers endows MST with the uniqueness that must be demanded of a proper physical theory. Thus, any other expression of the MST equations, which can be shown to be inequivalent to those of the MT form must be either approximate or incorrect.

At this point, we have succeeded in reaching our goal of justifying the use of the MT form of MST in connection with non-MT, space-filling potentials. In the next section we continue our exposition of MST for generally shaped potentials and provide explicit expressions for a number of physically important quantities.

IV. Green Functions, Bloch Functions and the Lloyd Formula

In this section we derive expressions for the Green function for general assemblies of scattering potentials and for the Bloch function for a periodic material, and provide a derivation of the Lloyd formula for the integrated density of states in the latter case. We show that the final expressions for all these quantities have precisely the same forms as those associated with MT potentials.

A. The Green Function for Non-MT Potentials

A particularly detailed account of MST for the case of MT potentials has been given by Butler[44] for the special case of one-dimensional systems, while a summary of the general formalism of MST for MT potentials in three-dimensions has been presented by Faulkner,[6] and other investigators.[16,26] In addition to extending the formalism of MST to potentials of arbitrary shape, we will also indicate that the formalism describing scattering of MT potentials is not completely immune from difficulties associated with the expansion of the free-particle propagator.

First, we consider the case of a finite collection of scattering centers and generalize to that of an infinite number of scatterers at the end. We note that for vectors $\mathbf{r}$ and $\mathbf{r}'$ outside a sphere covering the *entire* assembly the Green function, Eq. (2.10), can be written in the angular momentum representation in the form (with $|\mathbf{r}'| > |\mathbf{r}|$)

$$
\begin{aligned}
G(\mathbf{r}, \mathbf{r}') &= -ik \sum_{L} J_L(\mathbf{r}) H_L(\mathbf{r}') - k^2 \sum_{LL'} H_L(\mathbf{r}) T_{LL'} H_{L'}(-\mathbf{r}') \\
&= \langle J(\mathbf{r}) \,|\, H(\mathbf{r}') \rangle + \langle H(\mathbf{r}) \,|\, \underset{\sim}{T} \,|\, H(-\mathbf{r}') \rangle \quad . \qquad (4.1)
\end{aligned}
$$

Here, we have used Eq. (A.6) and the vector/matrix notation introduced in the appendix, and have also associated a factor of $-ik$ with the Hankel functions. We now insert the expression for $\underset{\sim}{T}$, Eq. (2.25), into Eq. (4.1) and use Eq. (A.9) to obtain

$$G(\mathbf{r},\mathbf{r}') = \langle J(\mathbf{r}) \,|\, H(\mathbf{r}')\rangle + \sum_{i,j} \langle H(\mathbf{r}) \,|\, \underset{\sim}{g}_i \underset{\sim}{\tau}^{ij} \underset{\sim}{g}_j^{\dagger} \,|\, H(-\mathbf{r}')\rangle$$

$$= \langle J(\mathbf{r}) \,|\, H(\mathbf{r}')\rangle + \sum_{i,j} \langle H(\mathbf{r} - \mathbf{R}_i) \,|\, \underset{\sim}{\tau}^{ij} \,|\, H(-\mathbf{r}' + \mathbf{R}_j)\rangle \quad , \tag{4.2}$$

because $\mathbf{r}$ and $\mathbf{r}'$ are larger than any vectors $\mathbf{R}_j$. Upon using the inherently convergent multiplication process defined in Eq. (3.3) we can expand the Hankel functions as follows,

$$|\, H(\mathbf{r} - \mathbf{R}_i)\rangle = \underset{\sim}{G}(\mathbf{R}_i) \odot |\, J(\mathbf{r})\rangle$$

$$\equiv \underset{\sim}{G}(\mathbf{R}_i) \odot \left[\prod_{j=1}^{N} \underset{\sim}{g}(\mathbf{a}_j) \left| J\left(\mathbf{r} - \sum_{j=1}^{N} \mathbf{a}_j \right) \right\rangle \right]$$

$$\equiv \left\{ \left[\underset{\sim}{G}(\mathbf{R}_i) \underset{\sim}{g}(\mathbf{a}_1) \right] \underset{\sim}{g}(\mathbf{a}_2) \ldots \right\} \underset{\sim}{g}(\mathbf{a}_N) \,|\, J(0)\rangle \quad , \tag{4.3}$$

where $\mathbf{r} = \sum_{i=1}^{N} \mathbf{a}_i$ and the vectors $\mathbf{a}_i$ are again chosen so that $|\, \mathbf{R}_i - \sum_{j=1}^{n-1} \mathbf{a}_j \,| > |\, \mathbf{a}_n \,|$ for all $1 \leq n \leq N$. With this interpretation we can write Eq. (4.2) in the form

$$G(\mathbf{r},\mathbf{r}') = \langle J(\mathbf{r}) | H(\mathbf{r}')\rangle + \sum_{i \neq 0} \langle H(\mathbf{r}) \,|\, \underset{\sim}{\tau}^{oi} \odot \underset{\sim}{G}^{io} \odot |\, J(-\mathbf{r}')\rangle$$

$$+ \sum_{j \neq 0} \langle J(\mathbf{r}) \,|\, \odot \underset{\sim}{G}^{oj} \odot \underset{\sim}{\tau}^{jo} \,|\, H(-\mathbf{r}')\rangle + \sum_{\substack{i \neq 0 \\ j \neq 0}} \langle J(\mathbf{r}) \,|\, \odot \underset{\sim}{G}^{oi} \odot \underset{\sim}{\tau}^{ij} \odot \underset{\sim}{G}^{jo} \odot |\, J(-\mathbf{r}')\rangle \quad , \tag{4.4}$$

which has precisely the form given by Butler[44] when that form is generalized to three-dimensions and the various products are interpreted in light of the process defined in Eq. (3.3). The products $G^{oi} \odot \tau^{io}$, etc., have a somewhat subtle interpretation. They can be justified upon the expansion of $\underset{\sim}{\tau}$ in terms of the cell scattering matrices, each of which is considered as a collection of spheres (approximating the potential cell to arbitrary accuracy). Thus, Eq. (4.4) represents a convergent expression independent of the order of multiplication (or summation over L). Having proved that $\underset{\sim}{\tau}$ is of the MT form, Eq. (2.29), we have the identities

$$\sum_{i\neq 0}\underset{\sim}{\tau}^{oi}\odot\underset{\sim}{G}^{io}=\underset{\sim}{\tau}^{oo}\underset{\sim}{m}^{o}-\underset{\sim}{1}\quad, \tag{4.5a}$$

$$\sum_{j\neq 0}\underset{\sim}{G}^{oj}\odot\underset{\sim}{\tau}^{jo}=\underset{\sim}{m}^{o}\underset{\sim}{\tau}^{oo}-\underset{\sim}{1} \tag{4.5b}$$

$$\begin{aligned}\sum_{i\neq 0}\sum_{j\neq 0}\underset{\sim}{G}^{oj}\odot\underset{\sim}{\tau}^{ij}\odot\underset{\sim}{G}^{jo}&=\underset{\sim}{m}^{o}(\underset{\sim}{\tau}^{oo}-\underset{\sim}{t}^{o})\underset{\sim}{m}^{o}\\&=\underset{\sim}{a}^{oo}\quad,\end{aligned} \tag{4.5c}$$

and Eq. (4.4) can be readily written in the form

$$\begin{aligned}G(\mathbf{r},\mathbf{r}')&=\langle J(\mathbf{r})\,|\,H(\mathbf{r}')\rangle+\langle H(\mathbf{r})\,|\,\underset{\sim}{t}^{o}\,|\,H(-\mathbf{r}')\rangle\\&\quad+\left[\langle J(\mathbf{r})|-ik\langle H(\mathbf{r})\,|\,\underset{\sim}{t}^{o}\right]\underset{\sim}{a}^{oo}\left[\,|\,J(-\mathbf{r}')\rangle-ik\underset{\sim}{t}^{o}|H(-\mathbf{r}')\rangle\,\right]\quad,\end{aligned} \tag{4.6}$$

where the origin of coordinates has been taken to be the center of the cell at 0, and the factor $-ik$ is separated from the Hankel function in order to conform with established notation in our subsequent discussion. We note that Eq. (4.6) represents a convergent expression in terms of ordinary products (or summations over L). We note also that the dependence of its derivation upon the concept of inherently convergent, stepwise multiplications may be necessary also in the case of MT potentials, if the interstitial region, i.e., the region outside the MT spheres, is of sufficiently elongated shape. Then, the products of the type $\underset{\sim}{G}(\vec{\mathbf{R}}_{ij})\,|\,J(-\mathbf{r})\,\rangle$, which arise in a straightforward derivation of Eq. (4.6) for the case of MT potentials may involve vectors $|\,\mathbf{r}\,|>|\,\mathbf{R}_{ij}\,|$ and are thus ill defined. However, the process defined by Eq. (3.3) completely removes all expansion difficulties allowing the unified treatment of MT and non-MT cases.

Now, using the continuity properties of the Green function, the variables $\mathbf{r}$ and $\mathbf{r}'$ can be moved arbitrarily close to the center of the cell at the origin, and Eq. (4.6) can be further manipulated[44] into the form (with $|\,\mathbf{r}'\,|>|\,\mathbf{r}\,|$)

$$G(\mathbf{r},\mathbf{r}')=\langle Z^{o}(\mathbf{r})\,|\,\underset{\sim}{\tau}^{oo}\,|\,Z^{o}(-\mathbf{r}')\rangle-\langle Z^{o}(\mathbf{r})\,|\,S^{o}(\mathbf{r}')\rangle\quad. \tag{4.7}$$

Here, the functions $|\,Z^{i}(\mathbf{r})\rangle$ and $|\,S^{i}(\mathbf{r})\rangle$ are those regular and irregular solutions of the

Schrödinger equation, which on the surface of *any* sphere bounding the *entire* potential at $\mathbf{R}_i$ join smoothly to the functions $|Z^i(\mathbf{r})\rangle \rightarrow \underset{\sim}{m}^i\,|J(\mathbf{r})\rangle - ik\,|H(\mathbf{r})\rangle$ and $|S^i(\mathbf{r})\rangle \rightarrow |J(\mathbf{r})\rangle$, respectively. At real energies, these functions can be made real. Upon using the formalism developed thus far and considering the vectors $\mathbf{r}$ and $\mathbf{r}'$ as measured from the centers of cells i and j, respectively, we can obtain for the Green function the more general expression

$$G(\mathbf{r},\mathbf{r}') = \langle Z^i(\mathbf{r})\,|\,\underset{\sim}{\tau}^{ij}\,|\,Z^j(-\mathbf{r}')\,\rangle + \delta_{ij}\big[\theta(r - r')\langle Z^i(\mathbf{r}')\,|\,S^i(\mathbf{r})\rangle + \theta(r' - r)\langle Z^i(\mathbf{r})\,|\,S^i(\mathbf{r}')\rangle\big] \;, \tag{4.8}$$

which is identical in form to the corresponding expression for MT potentials. We easily realize that Eq. (4.8) remains valid as the number of scatterers increases beyond bound.[45] Thus, this expression provides the explicit means for calculating charge densities and local densities of states, in finite clusters or materials of infinite extent, and can be used in the performance of self-consistent electronic structure calculations and the calculation of total energies, for both pure materials and substitutionally disordered alloys.

For the special case of materials possessing translational invariance, the electronic structure, E(**k**), can be obtained from the poles of the t-matrix in reciprocal space, that is to say as the solutions of the secular equation

$$|\,\underset{\sim}{m} - \underset{\sim}{G}(\mathbf{k})\,| = 0 \;. \tag{4.9}$$

Here, $|\,\underset{\sim}{A}\,|$ denotes the determinant of a matrix , $\underset{\sim}{A}$, $\underset{\sim}{m}$ is the inverse of the full cell scattering matrix, and the $\underset{\sim}{G}(\mathbf{k})$ are the **k**-space representatives of the free-particle propagator for the lattice (KKR structure constants). This expression is, of course, identical to that used in the case of MT potentials.

B. Bloch Functions for Lattice Periodic Systems

It is now a simple matter to derive an expression for the Bloch function of a periodic material. Neglecting[46] the (real) single-scatterer term for real values of the energy, we obtain after a Fourier transformation of Eq. (4.7),

$$\underset{\sim}{G}_{\mathbf{k}}(\mathbf{r}, \mathbf{r}') = \langle Z(\mathbf{r}) | \underset{\sim}{\tau}(\mathbf{k}) | Z(-\mathbf{r}') \rangle \quad , \tag{4.10}$$

where $\mathbf{r}$, $\mathbf{r}'$ are cell vectors. By definition, the Bloch functions $| \phi_{\mathbf{k}}(\mathbf{r}) \rangle$ diagonalize $G_{\mathbf{k}}(\mathbf{r},\mathbf{r}')$ by means of the relation,

$$G_{\mathbf{k}}(\mathbf{r}, \mathbf{r}') = \langle \phi_{\mathbf{k}}(\mathbf{r}) | [E - E(\mathbf{k})]^{-1} | \phi_{\mathbf{k}}(-\mathbf{r}') \rangle \quad . \tag{4.11}$$

It follows that

$$| \phi_{\mathbf{k}}(\mathbf{r}) \rangle = \underset{\sim}{C}(\mathbf{k}) | Z(\mathbf{r}) \rangle \tag{4.12}$$

where $\underset{\sim}{C}(\mathbf{k})$ is the matrix that diagonalizes $\underset{\sim}{\tau}(\mathbf{k})$. Again, we note that Eq. (4.12) has precisely the form defining the Bloch function in the case of MT potentials.

An expression for the cell charge density can now be obtained. By definition, at energy, E, we have

$$\begin{aligned} \rho_E(\mathbf{r}) &= -\frac{1}{\pi} \operatorname{Im} \operatorname{Tr} G(\mathbf{r}, \mathbf{r}') \\ &= -\frac{1}{\pi}\frac{1}{\Omega_{BZ}} \int d^3k \, \langle Z(\mathbf{r}) | \operatorname{Im} \underset{\sim}{\tau}(\mathbf{k}) | Z(-\mathbf{r}) \rangle \quad . \end{aligned}$$

Using Eq. (4.12) we obtain the well-known and general expression

$$\rho_E(\mathbf{r}) = \frac{1}{\Omega_{BZ}} \int_{BZ} d^3k \, \langle \phi_{\mathbf{k}}(\mathbf{r}) | \phi_{\mathbf{k}}(-\mathbf{r}) \rangle \quad , \tag{4.13}$$

where the integration extends over the first Brillouin zone (BZ) of the reciprocal lattice, whose volume is denoted by Ω_{BZ}. The charge density follows upon integration over the energy, whereas the density of states is given by an integral over the coordinates, $\mathbf{r}$.

C. The Lloyd Formula

The change in the integrated density of states, $\Delta N(E)$, resulting from the introduction of a single scatterer into otherwise free space is given[30,47,48] by the expression,

$$\Delta N(E) = -\frac{1}{\pi} \mathrm{Im}\, \mathrm{Tr} \ln \underset{\sim}{T}$$

$$= -\frac{1}{\pi} \mathrm{Im} \ln | \underset{\sim}{T} | \quad . \tag{4.14}$$

For a translationally invariant material, it is convenient to define the change in the integrated DOS corresponding to a unit cell,

$$\Delta \hat{N}(E) \equiv \Delta N(E)/N \quad , \tag{4.15}$$

where N denotes the number of unit cells comprising the material. In general, the quantity $\underset{\sim}{T} = < \underset{\sim}{g} \,|\, \underset{\sim}{\tau} \,|\, \underset{\sim}{g}^{\dagger} >$ can also be written in terms of the Fourier transforms, $\underset{\sim}{g}(\mathbf{k})$ and $\underset{\sim}{\tau}(\mathbf{k},\mathbf{k}')$, defined in the usual way, as follows,

$$\underset{\sim}{T} = \sum_{\mathbf{k},\mathbf{k}'} \underset{\sim}{g}(\mathbf{k})\, \underset{\sim}{\tau}(\mathbf{k},\mathbf{k}')\, \underset{\sim}{g}^{\dagger}(\mathbf{k}')$$

$$= <\underset{\sim}{g} \,|\, \underset{\approx}{\tau} \,|\, \underset{\sim}{g}^{\dagger}>_{\mathbf{k}} \quad , \tag{4.16}$$

where $\underset{\approx}{\tau}$ is a block matrix with elements $\underset{\sim}{\tau}(\mathbf{k},\mathbf{k}')$ and the subscript $\mathbf{k}$ keeps track of the representation. Now, upon augmenting the vectors $|\underset{\sim}{g}>_{\mathbf{k}}$ and $<\underset{\sim}{g}|_{\mathbf{k}}$ to matrices, $\underset{\approx}{g}$ and $\underset{\approx}{g}^{\dagger}$, analogously to the treatment of Eq. (3.6), and noting that the imaginary parts of the logarithms of the determinants of $\underset{\approx}{g}$ and $\underset{\approx}{g}^{\dagger}$ have opposite signs, we obtain,

$$\Delta \hat{N}(E) = -\frac{1}{\pi N} \mathrm{Im} \ln \det \underset{\approx}{\tau} \quad . \tag{4.17}$$

Furthermore, for a translationally invariant material, $\underset{\approx}{\tau}$ is a block diagonal $N \times N$ matrix, with each block corresponding to a $\mathbf{k}$ vector in the first Brillouin zone and given by $\underset{\sim}{\tau}(\mathbf{k})$, so that Eq. (4.17) can be written as

$$\Delta \hat{N}(E) = -\frac{1}{\pi N} \mathrm{Im} \ln \prod_{\mathbf{k} \in BZ} \det \underset{\sim}{\tau}(\mathbf{k})$$

$$= -\frac{1}{\pi}\,\mathrm{Im}\,\frac{1}{N}\sum_{\mathbf{k}\in BZ} \ln \det \underset{\sim}{\tau}(\mathbf{k})$$

$$= -\frac{1}{\pi}\,\mathrm{Im}\,\frac{1}{\Omega_{BZ}}\int_{BZ} \ln \det \underset{\sim}{\tau}(\mathbf{k})\, d^3\mathbf{k} \quad . \tag{4.18}$$

The last expression is the well-known[49] Lloyd formula for the integrated density of states corresponding to a periodic material.

V. Numerical Results

In this section we report the results of numerical investigations which address various aspects of the formalism presented in the previous sections. Because the proof that the scattering matrix remains invariant under a shift of the cell centers, Section III B, depends critically on the convergence properties of products involving the expansion coefficients,[50] $\underset{\sim}{g}(\mathbf{a})$, we evaluated numerically a number of products involving these coefficients. The results of these tests are shown in Figs. 1 and 2. In Fig. 1 we summarize the results obtained in the evaluation of the product $[\underset{\sim}{g}(\mathbf{a})\ \underset{\sim}{g}(-\mathbf{a})]_{LL}$ with (L,L) indicated in parentheses, as a function of L_{max}, the largest value of the angular momentum used in the internal summations. The values of the real parts of the products

$$\left[\underset{\sim}{g}(\mathbf{a})\ \underset{\sim}{g}(-\mathbf{a})\right]_{LL} = \sum_{L'=0}^{L_{max}} g_{LL'}(\mathbf{a})\, g_{L'L}(-\mathrm{a}) \tag{5.1}$$

are compared against their converged value of unity, Eq. (A.16), for the vectors $\mathbf{a} = (1, 0, 0)$, 2**a**, 3**a**, and 4**a** in panes (a) through (d), respectively. As is seen in these figures, the rate of convergence at fixed L_{max} is decreasing with increasing value of $|\mathbf{a}|$, but convergence can always be expected at fixed $|\mathbf{a}|$, with increasing value of L_{max}. The convergence to zero of the off-diagonal elements of the product $\underset{\sim}{g}(\mathbf{a})\ \underset{\sim}{g}(-\mathbf{a})$, not shown, exhibits similar behavior. Figure 2 depicts the convergence of product $\underset{\sim}{g}(\mathbf{a})\, \underset{\sim}{G}(\mathbf{R}) = \underset{\sim}{G}(\mathbf{R} - \mathbf{a})$, $|\mathbf{R}| > |\mathbf{a}|$. Here, we plot

$$\Delta_{LL} = \left|\left[\underset{\sim}{g}(a)\,\underset{\sim}{G}(2a) - \underset{\sim}{G}(a)\right]_{LL}\right| / \left|G_{LL}(a)\right| \tag{5.2}$$

for L = 0 and L = 1, against the value of L_{max}. Again, the convergence to zero with increasing L_{max} is evident.

The results shown in Figs. 1 and 2 illustrate the validity of the algebraic manipulations leading to the vanishing of NFCs, presented in Section III. From a practical standpoint, we note that in realistic bandstructure calculations, say for elements of the transition series, the value of ka ($k = \sqrt{E}$, a = lattice constant) is of the order of ~4.0 or less, and thus no serious convergence problems ought to be expected in this case.

The vanishing of NFCs in certain cases is illustrated by the results of the cluster calculations shown in Figs. 3 through 5. In these figures we compare the values of the total scattering matrix, $\underset{\sim}{T}$, associated with a spatially bounded potential, obtained with the potential partitioned into cells in two different ways. Figure 3 depicts a schematic diagram of a potential consisting of three MT scatterers, part (a), viewed as two-scatterer problem with two of the scatterers taken to comprise a single cell centered at point 0, part (b). The exact total t-matrix, $\underset{\sim}{T}_{ex}$, of this collection of scatterers can be obtained from Eq. (2.25), with $\underset{\sim}{T}^{ij}$ in that equation being given by the inverse of the MT matrix, Eq. (2.29), corresponding to the three MT scatterers shown in part (a). This value can then be compared to that obtained under the following two-step process: First, the t-matrix corresponding to a cell consisting of two MT potentials treated as a unit is calculated and second, that t-matrix and the t-matrix corresponding to the third cell are combined through the MT equations, (2.25) and (2.29). Because a sphere centered at the center of the combined cell and bounding that cell may overlap with the third MT potential, the presence of NFCs can be directly associated with any differences in the total scattering matrix, $\underset{\sim}{T}$, obtained in these two ways. Figure 4 shows the convergence of the quantities $(|T| - |T_{ex}|)/|T_{ex}|$ associated with two values of ℓ, $\ell = 0$ (solid curve) and $\ell = 1$ (dashed curve), for the case in which the three scatterers were characterized by the single phase shift, $\delta_0 = 0.1$, and were linearly arranged at distance a = 1 apart, so that a sphere bounding the combined cell also included the third scatterer. The convergence to the exact value with increasing value of ℓ in the angular momentum expansions is evident in this figure. A similar rate of convergence is shown in Fig. 5 for the case[43] of four scatterers arranged linearly, characterized by the phase shifts $\delta_0 = 0.1$ and $\delta_1 = 0.2$, with three of them combined into a single cell whose bounding sphere contained completely the remaining fourth cell. Here, the convergence of the $\ell = 1$ component of $\underset{\sim}{T}$ is shown, and is seen to behave quite similarly to the convergence depicted in Fig. 4. These figures clearly illustrate the vanishing of NFCs in this case and, in addition, their similarity suggests that any deviation from exact results is simply due to the lack of convergence of the angular momentum expansions.

The question of convergence of the angular momentum expansions in realistic bandstructure calculations is illustrated in Figs. 6 through 8, in terms of the bandstructures of elemental bcc Nb, and fcc Rh and Zr. The potentials used in these calculations were simply constructed according to the Mattheiss[51] prescription from atomic potentials obtained in the local density approximation (LDA)[52] for the nominal configurations of the various atoms. The first step in this construction is to obtain the overlapped election density,

$$\rho(\mathbf{r}) = \sum_i \rho_A(\mathbf{r} - \mathbf{R}_i) \quad , \tag{5.3}$$

where $\rho_A(\mathbf{r} - \mathbf{R}_i)$ is the charge density contributed by the atom at point $\mathbf{R}_i$. The resulting potential includes the Coulomb contributions of the electron and nuclear charge densities, and the full Slater approximation to the exchange,

$$V(\mathbf{r}) = \int \frac{2\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r' - 2 \sum_i \frac{2Z_i}{|\mathbf{r} - \mathbf{R}_i|} - 6\left[\frac{3}{8}\pi \rho_f(\mathbf{r})\right]^{1/3} \quad . \tag{5.4}$$

The individual cell potentials V_i are given by

$$V_i(\mathbf{r}) = V(\mathbf{r})\,\theta_i(\mathbf{r}) \tag{5.5}$$

where the shape function $\theta_i(\mathbf{r})$ restricts the potential to the i^{th} cell,

$$\theta_i(\mathbf{r}) = \begin{cases} 1 & \text{if } \mathbf{r} \text{ is inside cell } i \\ 0 & \text{otherwise} \end{cases} \quad . \tag{5.6}$$

The Mattheis procedure is known to give reasonable bands and is a commonly used approach to obtaining starting potentials for LDA bandstructure calculations. We note that the expressions for the Green function and the integrated density of states derived in Section IV provide the necessary machinery for proceeding to self-consistency. However, the continuation to self-consistency would be an unnecessary distraction in this discussion, whose focus is the solution of the Schrödinger equation for a *given* potential of arbitrary shape. Furthermore, in practice a linear or quadratic approximation^{53} to the MST equations for all but the simplest systems would be employed for the iteration of the local density equations. The present discussion of NFCs would be pertinent to such methods because these involve scattering from potentials whose bounding spheres overlap over regions in which the potential can be as large as 1 Ry. In fact, the proof that NFCs vanish provides the rigorous justification for the use of these techniques.

In the following figures we show the bandstructures of various elemental solids obtained through the use of Eq. (4.9) in which the (inverse) single-site scattering matrix is given by

$$\underset{\sim}{m} = -\sqrt{E}\left(\underset{\sim}{C}\,\underset{\sim}{S}^{-1} - i\right) \tag{5.7}$$

or explicitly,

$$m_{LL'} = -\sqrt{E}\left(\sum_{L_1} C_{LL_1}\left[S^{-1}\right]_{L_1L'} - i\right) \tag{5.8}$$

where the cell phase functions $\underset{\sim}{C}$ and $\underset{\sim}{S}$ are evaluated at points outside the sphere bounding a cell. These functions are obtained through the expressions, (see Eqs. (2.3a) and (2.27)),

$$\underset{\sim}{C} = \int |\phi(\mathbf{r})\rangle \, V(\mathbf{r}) \, \langle N(\mathbf{r})| \, d^3 r \quad , \tag{5.9a}$$

$$\underset{\sim}{S} = \int |\phi(\mathbf{r})\rangle \, V(\mathbf{r}) \, \langle J(\mathbf{r})| \, d^3 r \quad , \tag{5.9b}$$

where $|\phi(\mathbf{r})\rangle$ is the solution of the equation (**r** outside the bounding sphere)

$$|\phi(\mathbf{r})\rangle = |J(\mathbf{r})\rangle + \int_{r'<r} K(\mathbf{r},\mathbf{r}') \, V(\mathbf{r}') |\phi(\mathbf{r}')\rangle \, d^3 r \quad , \tag{5.10}$$

for the cell potential, V, with the kernel, K, being the free-particle propagator

$$K(\mathbf{r},\mathbf{r}') = -\sqrt{E}\,[\,\langle J(\mathbf{r})|N(\mathbf{r}')\rangle\,\theta(r'-r) - \langle N(\mathbf{r})|J(\mathbf{r}')\rangle\,\theta(r-r')] \quad . \tag{5.11}$$

This results in a matrix of order $(2\ell_{max} + 1)^2$ whose determinant yields the band structure through Eq. (4.9).

Figure 6 depicts the bandstructure of elemental bcc Nb obtained from Eq. (4.9), (solid curves), compared to the results of the Discrete Variational Method (DVM)[54] as applied by Painter, Faulkner, and Stocks (PFS) in which the potential outside the inscribed (MT) spheres was taken into account in a perturbative way. Although the potentials used in these two calculations were not identical, they are very similar, both being calculated through the Mattheiss prescription. The bands of PFS have been previously found to agree closely with those obtained[55] through the use of the full potential linearized augmented plane wave method (FLAPW). The large degree of similarity between the full potential MST results (solid curve) and those of the DVM calculations shown here indicates that ℓ convergence has been reached in these calculations for Nb carried out to $\ell_{max} = 4$.

A more detailed study of convergence is presented in Fig. 7 for elemental fcc Rh. Here, the panels (a) through (d) correspond to the bandstructure obtained with $\ell_{max} = 1$, 2, 3, and 4, respectively. It is seen that the rate of the ℓ convergence for these full potential calculations is exceedingly rapid, being essentially complete at $\ell_{max} = 2$, panel (b), with higher values of ℓ adding little if anything to the bandstructure. Such rates of convergence are known to occur in the MT approximation to the cell potentials, and are shown here for the first time to exist in the case of full cell potentials as well. Clearly, expanding to values of ℓ higher than 4 is unwarranted, at least for the case of close packed structures. (We note that higher values of ℓ could in fact be taken into account through partitioning schemes,[54] which do not result in an increase of the dimensionality of the MST matrix, Eq. (4.9), and cost very little in computational time.) Finally, the bandstructure for elemental fcc Zr calculated with $\ell = 4$ is shown in Fig. 8.

In closing this section, we note that the calculations just presented attest to the feasibility of solving the MST equations in connection with full cell potentials, and indicate the rather rapid convergence of such calculations in angular momentum at least for the case of materials based on close packed crystal structures. The question of convergence in connection with more open or less symmetric structures clearly remains open, and should be addressed numerically on a case by case basis. However, in all such future calculations it should be borne in mind that any discrepancies from exact results should be attributed solely to the lack of convergence, and not on the existence of fundamental defects of MST, such as NFCs.

VI. Conclusions

In this paper we have shown that the muffin-tin form of the equations of multiple scattering theory is rigorously valid in all cases of nonoverlapping potential cells of arbitrary shape. Specifically, we have shown that near-field corrections vanish identically in all cases. Coupled with Zeller's demonstration that MST in the MT form satisfies the empty lattice test, the discussion in the body of the paper shows that this form of MST satisfies all three criteria discussed in Section II. Although recent work, see Section II, has indicated that as a matter of practicality NFCs could be ignored as small in all cases studied and could even be shown to vanish under certain conditions,[40] their vanishing in all cases regardless of the shape of the potential cells is an indispensible requirement to the logical structure of multiple scattering theory. As was pointed out in the body of the paper, the existence of finite NFCs depending on the partition of a given potential into cells (representation) and on the choice of cell centers (coordinate system) would demote MST to a level much lower than that of a fully satisfactory physical theory. It is gratifying to know that this is indeed *not* the case.

The vanishing of NFCs has also been illustrated by means of numerical examples in terms of cluster calculations and the determination of the electronic structure of several elemental solids. These calculations, although not proving the vanishing of NFCs, suggest that the ℓ convergence of realistic electronic structure calculations with full cell, non-MT potentials can be fairly rapid, requiring a value of the maximum angular momentum no larger than that needed for an accurate representation of the cell t-matrix. We might then anticipate that calculations involving open structure, e.g., diamond, would not require a value of L_{max} larger than say 6 or 8 for convergence. In any case, even if such calculations prove to converge quite slowly, the lack of convergence should be attributed to the insufficiently large value of L_{max}, and not to any fundamental defect of MST, such as NFCs.

In closing, we emphasize that an application of MST to full potential cell scattering has been shown to be rigorously valid, and the machinery has been established whereby one can perform fully self-consistent calculations for pure elemental solids, compounds, impurities and alloys. In a future publication it will be shown that this generalized form of MST allows the exact treatment of a number of low symmetry systems, such as surfaces and grain boundaries involving arbitrary lattice structures, as well as impurities near surface and grain boundary regions, within a unified formalism that is on a par with the calculations of the electronic structure of ordered materials. Further calculations using the full potential MST described here are under way and will be reported in forthcoming publications.

Acknowledgment

The authors are grateful to G. S. Painter for making available to them the results of the KKR-DVM calculations. The authors are also grateful to W. H. Butler and J. W. Garland for a number of helpful discussions and comments. This work was partly supported by the U.S. Department of Energy under contract No. W-7405-Eng-48 with Lawrence Livermore National Laboratory, and No. DE-AC05-840R21400 with Martin Marietta Energy Systems.

Appendix A

1. Translation Properties of Spherical Functions

Much of the formalism presented in the body of the paper rests on certain useful expansions[50] under displacement of the spherical functions, i.e., products of Bessel, Neumann and Hankel functions, $j_\ell(kx)$, $n_\ell(kx)$, and $h_\ell(kx)$, respectively, with the spherical harmonics $Y_L(x)$. In the following discussion such products will be denoted by $A_L(x) \equiv \alpha_\ell(kx)\, Y_L(\hat{x})$, where α_ℓ is either j_ℓ, n_ℓ or h_ℓ, L (= ℓ, m) is a composite angular momentum index, and $Y_L(\hat{x})$ can be taken to signify either the usual spherical harmonics or combinations of them chosen to be real. We are interested in expressions connecting the values $A_L(\mathbf{x} - \mathbf{a})$ about a displaced origin to the undisplaced values $A_L(\mathbf{x})$.

We begin with the expansion of a plane wave in terms of spherical functions using Bauer's identity,

$$
\begin{aligned}
e^{i\mathbf{k}\cdot\mathbf{r}} &= 4\pi \sum_{\ell,m} i^{\ell}\, j_\ell(kr)\, Y_{\ell,m}(\mathbf{r})\, Y^{*}_{\ell,m}(\hat{k}) \\
&= 4\pi \sum_{L} i^{\ell}\, J_L(\mathbf{r})\, Y^{*}_{L}(\hat{k}) \\
&= 4\pi \sum_{L} i^{-\ell}\, J_L(\mathbf{r})\, Y_{L}(\hat{k}) \qquad \text{(A.1)}
\end{aligned}
$$

Thus, for any vectors $\mathbf{r}$ and $\boldsymbol{\rho}$ we obtain

$$e^{i\mathbf{k}\cdot(\mathbf{r}+\boldsymbol{\rho})} = (4\pi)^2 \sum_{L_2}\sum_{L_3} i^{\ell_3-\ell_2} J_{L_2}(\mathbf{r})\, J_{L_3}(\boldsymbol{\rho})\, Y_{L_2}(\hat{\mathbf{k}})\, Y_{L_3}(\hat{\mathbf{k}})$$

$$= 4\pi \sum_{L_1} i^{-\ell_1} J_{L_1}(\mathbf{r}+\boldsymbol{\rho})\, Y_{L_1}(\hat{\mathbf{k}}) \quad . \tag{A.2}$$

Multiplying the equality formed by the last two expressions by $Y_{L_1}(\hat{\mathbf{k}})$ and integrating over the angles of $\hat{\mathbf{k}}$ we obtain the result

$$J_{L_1}(\mathbf{r}+\boldsymbol{\rho}) = 4\pi \sum_{L_2}\sum_{L_3} i^{\ell_1-\ell_2+\ell_3} C(L_1L_2L_3)\, J_{L_3}(\boldsymbol{\rho})\, J_{L_2}(\mathbf{r})$$

$$= \sum_{L_2} g_{L_1L_2}(\boldsymbol{\rho})\, J_{L_2}(\mathbf{r}) \tag{A.3}$$

Here,

$$C(L_1L_2L_3) = \int d\Omega Y_{L_1}(\Omega)\, Y_{L_2}(\Omega)\, Y_{L_3}(\Omega) \tag{A.4}$$

are Gaunt numbers, and the expansion coefficients in Eq. (A.3) are defined by the expression

$$g_{L_1L_2}(\boldsymbol{\rho}) = 4\pi \sum_{L_3} i^{\ell_1-\ell_2+\ell_3} C(L_1L_2L_3)\, J_{L_3}(\boldsymbol{\rho}) \quad . \tag{A.5}$$

These coefficients form a unitary matrix as is shown below, Eq. (A.16).

Equation (A.3) is the desired expression for the "shifted" function $J_L(\mathbf{r}+\boldsymbol{\rho})$ in terms of unshifted quantities $J_L(\mathbf{r})$, and it is valid for all vectors $\mathbf{r}$ and $\boldsymbol{\rho}$.

In order to derive an analogous result for the Hankel functions of the first kind, $H_L(\mathbf{r})$, we recall the usual expression for the outgoing free-particle propagator,

$$G_0(\mathbf{r},\mathbf{r}') = -\frac{1}{4\pi}\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}$$

$$= -\,i\,k \sum_{L} H_L(\mathbf{r}')\, J_L(\mathbf{r}), \qquad \text{for } |\,\mathbf{r}'\,| > |\,\mathbf{r}\,| \quad . \tag{A.6}$$

For any vectors $|\,\mathbf{R}\,| > |\,\mathbf{r}\,|$ there exist vectors $\boldsymbol{\rho}$ that satisfy the conditions $|\,\mathbf{R}\,| > |\,\mathbf{r}\,|$, $|\,\mathbf{R}\,| > |\,\mathbf{r} - \boldsymbol{\rho}\,|$ and $|\,\mathbf{R} - \mathbf{r}\,| > |\,\boldsymbol{\rho}\,|$, but are otherwise arbitrary so that we can write

$$-\frac{1}{4\pi}\frac{e^{ik|\mathbf{R} - \mathbf{r} + \boldsymbol{\rho}|}}{|\mathbf{R} - \mathbf{r} + \boldsymbol{\rho}|} = -\,i\,k \sum_{L_2} H_{L_2}(\mathbf{R})\, J_{L_2}(\mathbf{r} - \boldsymbol{\rho})$$

$$= -\,i\,k \sum_{L} H_L(\mathbf{R} - \mathbf{r})\, J_L(-\,\boldsymbol{\rho}) \quad . \tag{A.7}$$

Upon using Eq. (A.3) we obtain from the last two expressions the equality,

$$\sum_{L} H_L(\mathbf{R} - \mathbf{r})\, J_L(-\,\boldsymbol{\rho}) = \sum_{L_2} H_{L_2}(\mathbf{R}) \sum_{L} g_{L_2 L}(\mathbf{r})\, J_L(-\,\boldsymbol{\rho}) \quad , \tag{A.8}$$

from which it follows that (recall that $\boldsymbol{\rho}$ is arbitrary)

$$H_{L_1}(\mathbf{R} - \mathbf{r}) = \sum_{L_2} H_{L_2}(\mathbf{R})\, g_{L_2 L_1}(\mathbf{r}) \quad ,$$

$$= \sum_{L_3} G_{L_1 L_3}(\mathbf{R})\, J_{L_3}(\mathbf{r}), \qquad \text{for } |\mathbf{R}\,| > |\mathbf{r}\,| \quad . \tag{A.9}$$

In the last equation we have defined the expansion coefficients,

$$G_{L_1 L_2}(\mathbf{R}) = 4\pi \sum_{L_3} i^{\ell_1 - \ell_2 + \ell_3}\, C(L_1 L_2 L_3)\, H_{L_3}(\mathbf{R}), \qquad |\mathbf{R}\,| \neq 0 \quad . \tag{A.10}$$

For values of $\mathbf{R}$ corresponding to the translation vectors of a regular lattice, the quantities $-\,ik\, G_{LL'}(\mathbf{R})$ are the real-space structure constants of the KKR method. Expressions similar to (A.9) hold for Neumann functions as well as the Hankel function of the second kind.

2. A Convenient Notation

Denoting row and column vectors by bras and kets, respectively, indexed by L we can write Eqs. (A.3) and (A.9) in the condensed forms

$$|\, J(\mathbf{r} + \boldsymbol{\rho})\rangle = \underset{\sim}{g}(\boldsymbol{\rho})\,|\, J(\mathbf{r})\rangle, \qquad \text{for all } \mathbf{r} \text{ and } \boldsymbol{\rho} \tag{A.11}$$

and

$$|\, H(\mathbf{R} - \mathbf{r})\,\rangle = \underset{\sim}{G}(\mathbf{R})\,|\, J(\mathbf{r})\,\rangle, \qquad \text{for } |\,\mathbf{R}\,| > |\,\mathbf{r}\,| \;, \tag{A.12}$$

where $\underset{\sim}{g}$ and $\underset{\sim}{G}$ denote the matrices whose elements are defined by Eqs. (A.5) and (A.10), respectively. Expressions analogous to Eqs. (A.11) and (A.12) in terms of bra's also exist. It is important to note that Eq. (A.12) is valid only if $|\,\mathbf{R}\,| > |\,\mathbf{r}\,|$; otherwise the summation in Eq. (A.9) cannot be shown to converge.

It is simple to derive a set of useful relations involving the various expansion coefficients $\underset{\sim}{g}$ and $\underset{\sim}{G}$. Using Eq. (A.9) we obtain

$$\begin{aligned} |\, H(\mathbf{r} - \mathbf{a} + \mathbf{a})\,\rangle &\equiv |\, H(\mathbf{r})\,\rangle \\ &= \underset{\sim}{G}(\mathbf{r} - \mathbf{a})\,|\, J(-\,\mathbf{a})\,\rangle, \quad \text{for } |\,\mathbf{r} - \mathbf{a}\,| > |\,\mathbf{a}\,| \end{aligned} \tag{A.13}$$

and also

$$\begin{aligned} |\, H(\mathbf{r} - \mathbf{a} + \mathbf{a})\,\rangle &= \underset{\sim}{G}(\mathbf{r})\,|\, J(\mathbf{a} - \mathbf{a})\,\rangle \\ &= \underset{\sim}{G}(\mathbf{r})\,[\underset{\sim}{g}(\mathbf{a})\,|\, J(-\,\mathbf{a})\,\rangle\,] \quad \text{for all } \mathbf{r} \text{ and } \mathbf{a} \;. \end{aligned} \tag{A.14}$$

Thus, for $|\,\mathbf{r}\,| > |\,\mathbf{a}\,|$ we find

$$\begin{aligned} \underset{\sim}{G}(\mathbf{r} - \mathbf{a}) &= \underset{\sim}{G}(\mathbf{r})\,\underset{\sim}{g}(\mathbf{a}) \\ &= \underset{\sim}{g}(\mathbf{a})\,\underset{\sim}{G}(\mathbf{r}) \;. \end{aligned} \tag{A.15}$$

Clearly, we also have the relations

$$\underset{\sim}{g}(\mathbf{a})\,\underset{\sim}{g}(-\,\mathbf{a}) = \underset{\sim}{1}$$

$$= \underset{\sim}{g}(\mathbf{a})\,\underset{\sim}{g}^{\dagger}(\mathbf{a}) \tag{A.16}$$

and

$$\underset{\sim}{g}(\mathbf{a})\,\underset{\sim}{g}(\mathbf{b}) = \underset{\sim}{g}(\mathbf{a} + \mathbf{b}), \quad \text{for all } \mathbf{a} \text{ and } \mathbf{b} \quad , \tag{A.17}$$

which can be derived in a straightforward manner.

Finally, for three vectors $\mathbf{r}_1$, $\mathbf{r}_2$ and R, which satisfy the conditions (the muffin-tin conditions),

$$|\,\mathbf{R}\,| > |\,\mathbf{r}_1\,|,\ |\,\mathbf{R}\,| > |\,\mathbf{r}_2\,|, \quad \text{and} \quad |\,\mathbf{R}\,| > |\,\mathbf{r}_1 - \mathbf{r}_2\,|,\ |\,\mathbf{R} - \mathbf{r}_2\,| > |\,\mathbf{r}_1\,|,$$
$$\text{and} \quad |\,\mathbf{R} + \mathbf{r}_1\,| > |\,\mathbf{r}_2\,| \tag{A.18}$$

we obtain the expression

$$G_0(\mathbf{R} - \mathbf{r}_1 + \mathbf{r}_2) = -\,ik\,\langle J(\mathbf{r}_1)\,|\,\underset{\sim}{G}(\mathbf{R})\,|\,J(-\,\mathbf{r}_2)\,\rangle \quad , \tag{A.19}$$

or explicitly,

$$G_0(\mathbf{R} - \mathbf{r}_1 + \vec{\mathbf{r}}_2) = -\,ik \sum_{LL'} J_L(\mathbf{r}_1)\,G_{LL'}(\mathbf{R})\,J_{L'}(-\,\mathbf{r}_2) \quad . \tag{A.20}$$

For lattice vectors R, the quantity $-\,ik\,\underset{\sim}{G}(\mathbf{R})$ is precisely the real-space representation of the KKR structure constant. In the text it is denoted by the same symbol, $\underset{\sim}{G}(\mathbf{R})$, in order to avoid proliferation of notation.

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31. The term "eigenstate" is used here in a nonrigorous sense since the $| X_\alpha >$ are not normalizable except in a δ-function sense. This purely formal and commonly employed representation, however, does not affect our final results.
32. The $\underset{\sim}{\tau}^{ij}$ are not proper operators in a Hilbert space, but rather the on-the-energy shell elements of the t-matrix operators $\underset{\sim}{T}^{\pm}$.
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45. One can always consider a sphere as enclosing any collection of scatterers, even those containing an infinite number of cells and the derivation of Eq. (4.8) is independent of the number of scattering centers.

46. The single scatterer term is complex at complex energies and must be taken into account in that case.

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Figure Captions

Figure 1. The convergence of the product $\underset{\sim}{g}(\mathbf{a})\,\underset{\sim}{g}(-\mathbf{a})$ for various values of $\mathbf{a}$ as a function of L_{max}, as described in the text.

Figure 2. The convergence of the product $[\underset{\sim}{g}(\mathbf{a})\,\underset{\sim}{G}(\mathbf{R})]_{LL}$ for $L = 0$ and $L = 1$ as a function of L_{max}, as described in the text.

Figure 3. Three MT scatterers, part (a), viewed as a two-scattering problem, part (b), with two of the scatterers treated as a single cell.

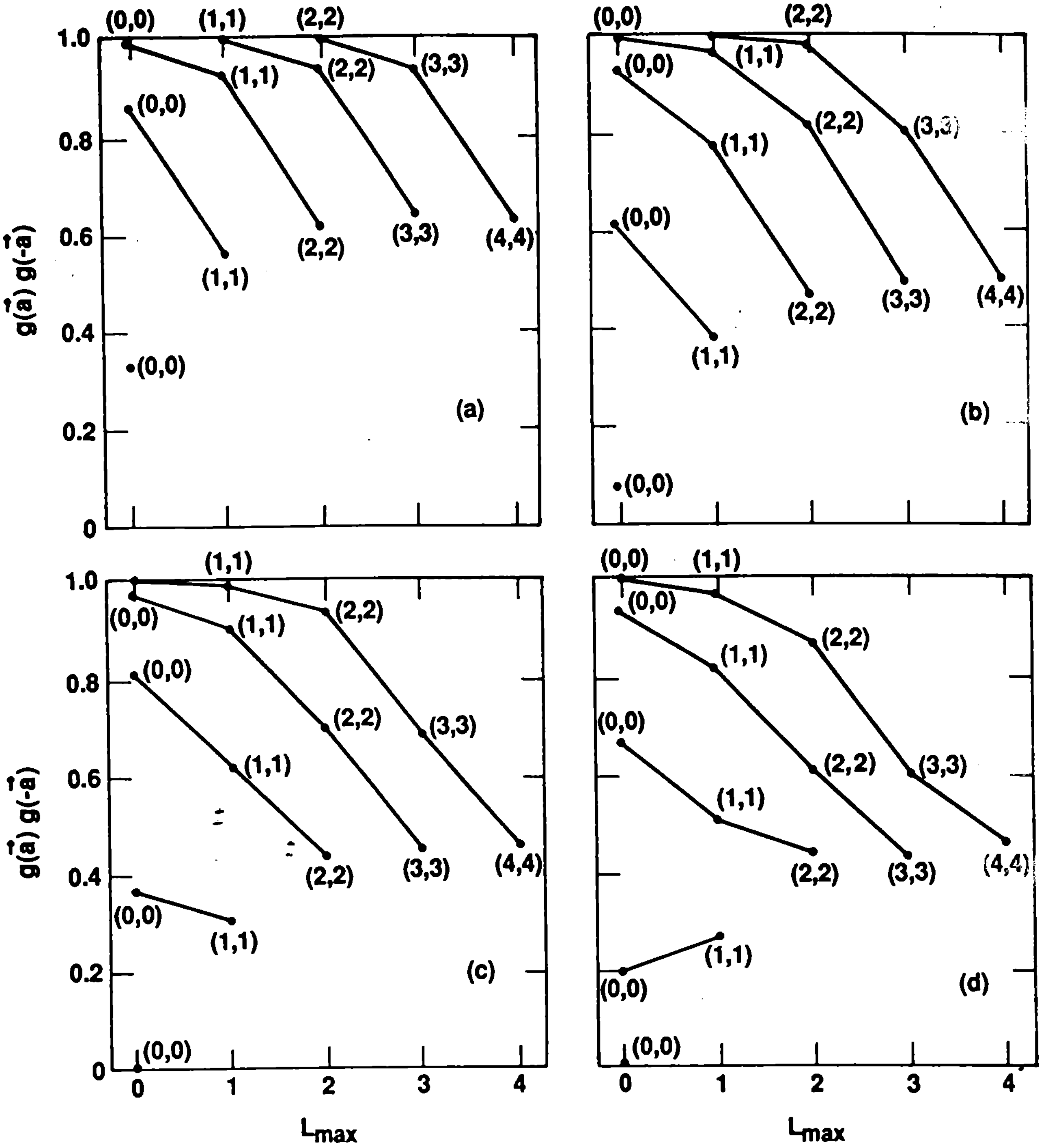
Figure 4. The convergence of the total t-matrix $\underset{\sim}{T}_{\ell\ell}$, for $\ell = 0$ and 1, for a three-scatterer assembly with two scatterers treated as a single cell.

Figure 5. The convergence of the total t-matrix, T_{11}, for a four scatterer assembly with three of the scatterers treated as a single cell.

Figure 6. The electronic bandstructure of elemental bcc Nb calculated within the full potential application of MST discussed in the text, (solid curves), compared with the results of a DVM calculation for similar non-MT potentials (dots).

Figure 7. The electronic bandstructure of elemental fcc Rh as a functional of ℓ, calculated using the full potential MST discussed in the text. Here, panels (a), (b), (c), and (d) correspond to $\ell = 1, 2, 3$, and 4.

Figure 8. The electronic bandstructure of elemental fcc Zr for $\ell = 4$ using the full potential MST discussed in the text.



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0.6
0.4
0.2
0
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0
1
2
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4
(0,0)
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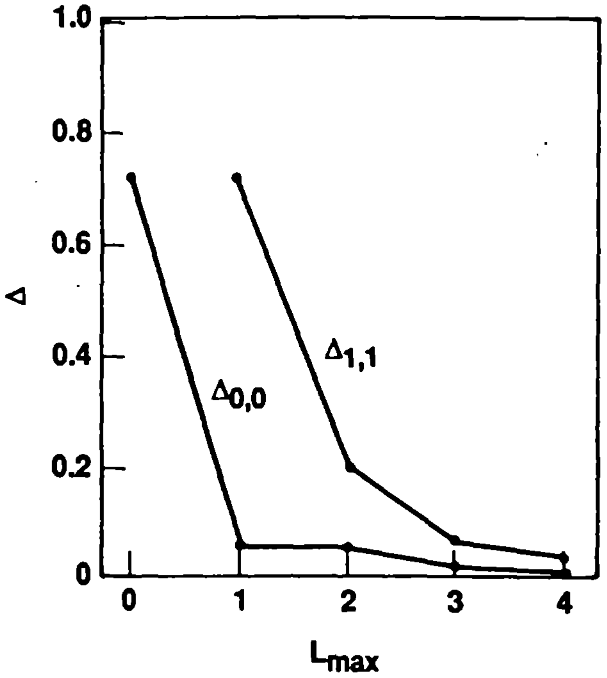
(3,3)
(4,4)
(a)
(b)
(c)
(d)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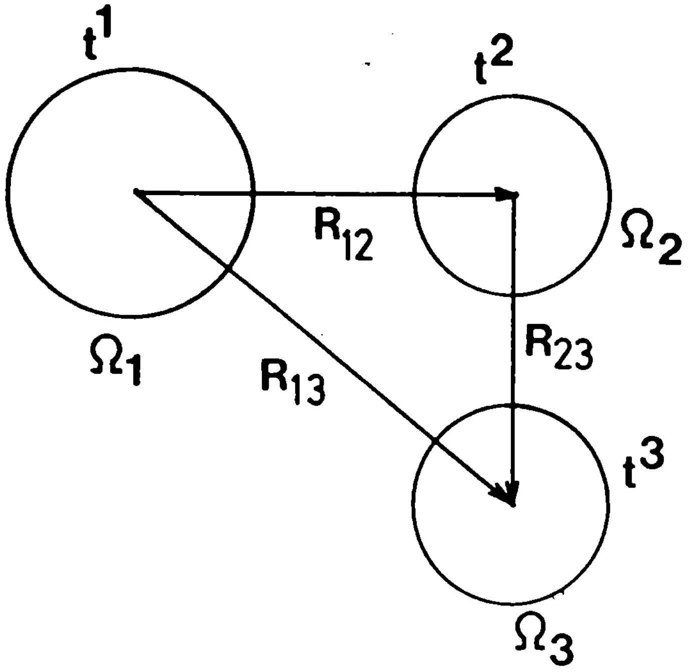
L_{max}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t^2
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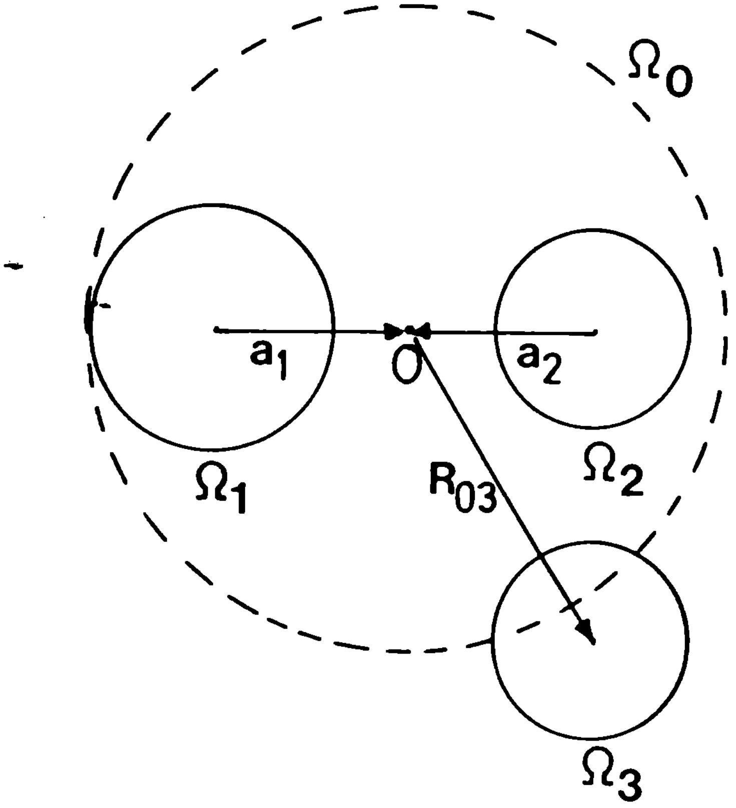
Ω_2
Ω_1
R_{13}
R_{23}
t^3
Ω_3

(a)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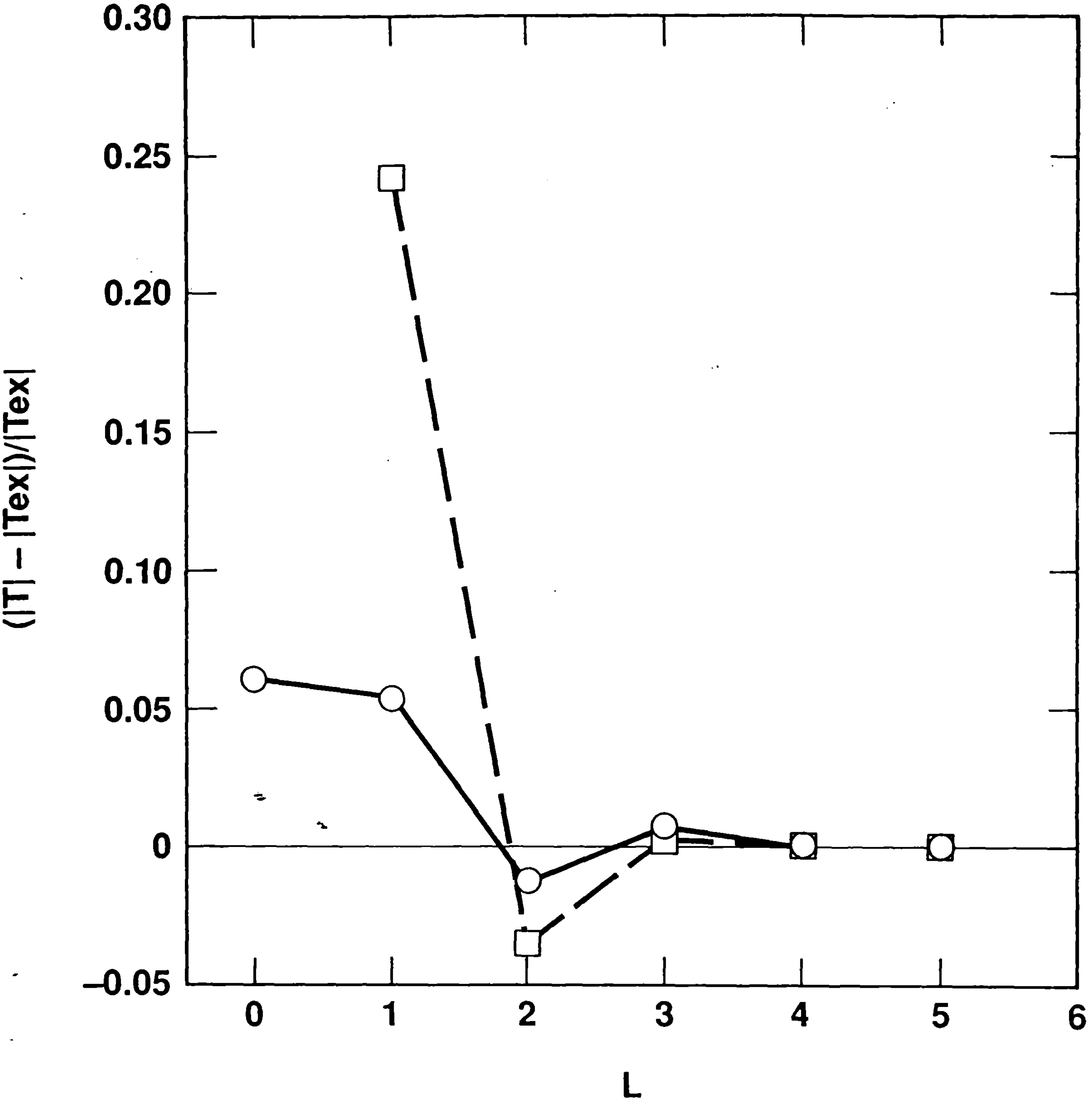
a_1
O
a_2
Ω_1
R_{03}
Ω_2
Ω_3

(b)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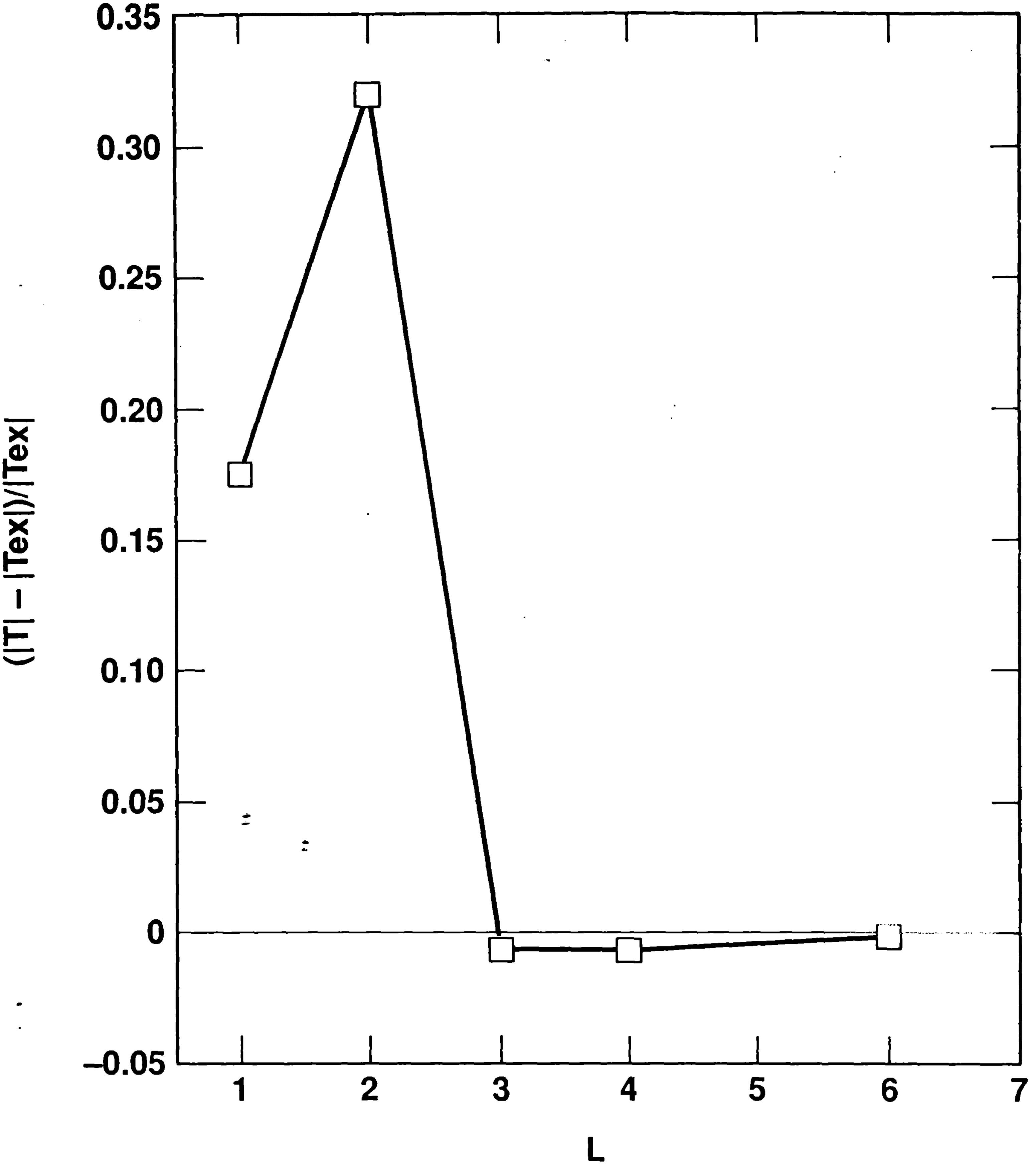

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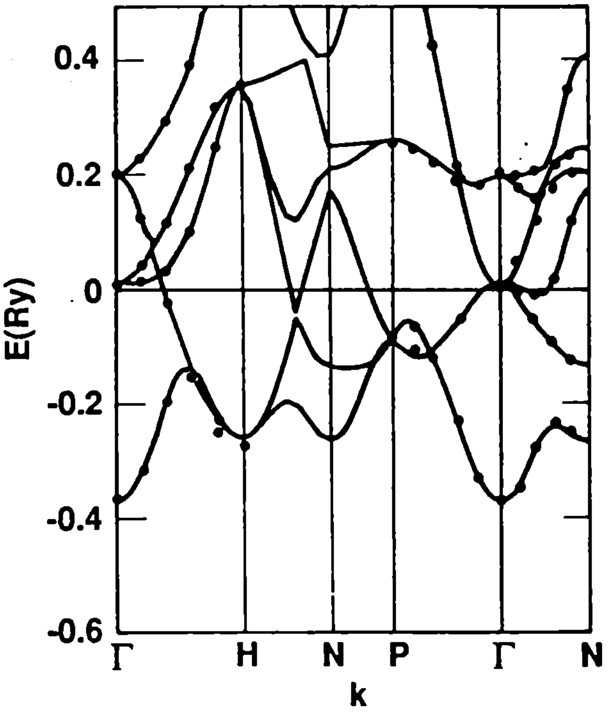
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E(Ry)
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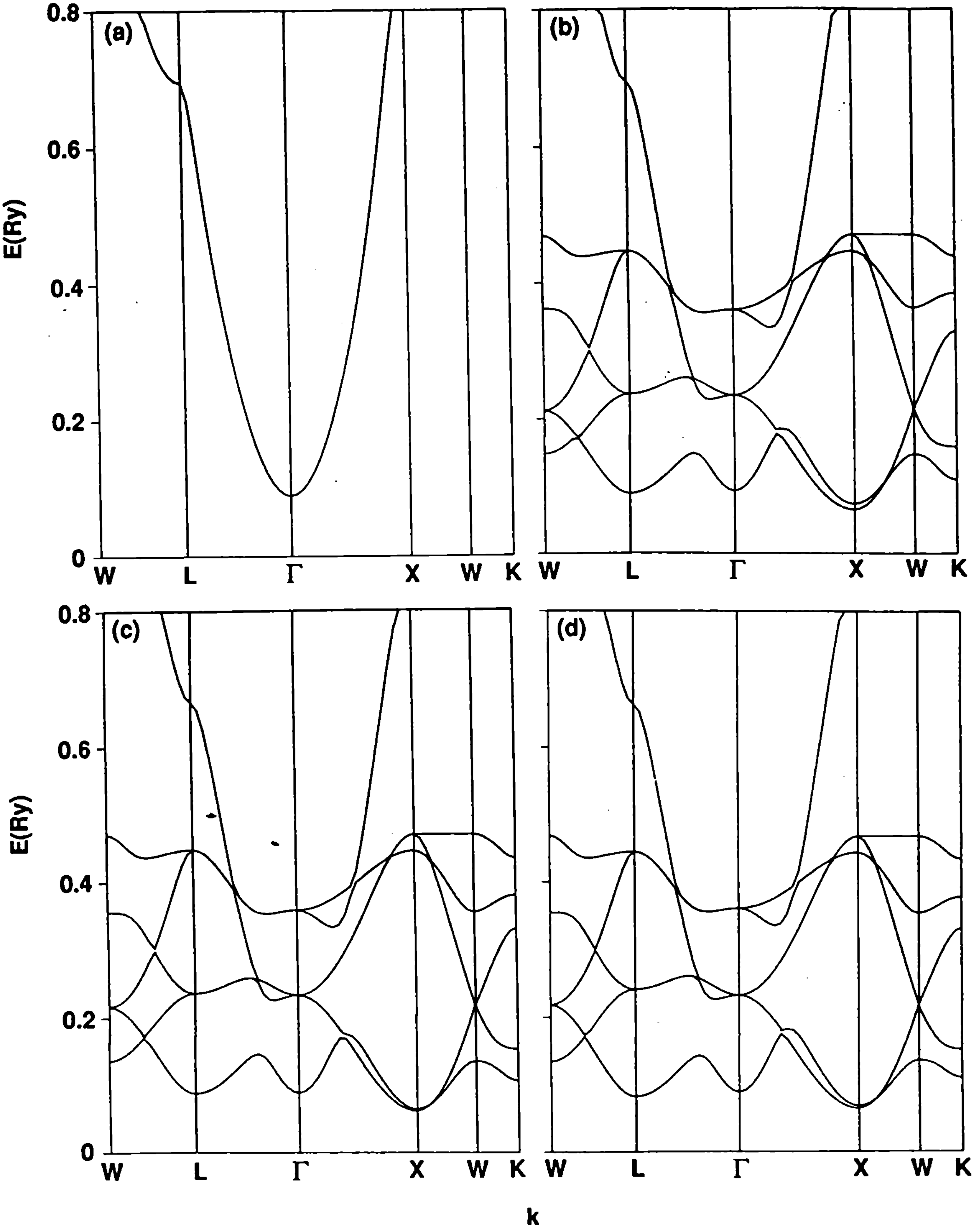

(a)
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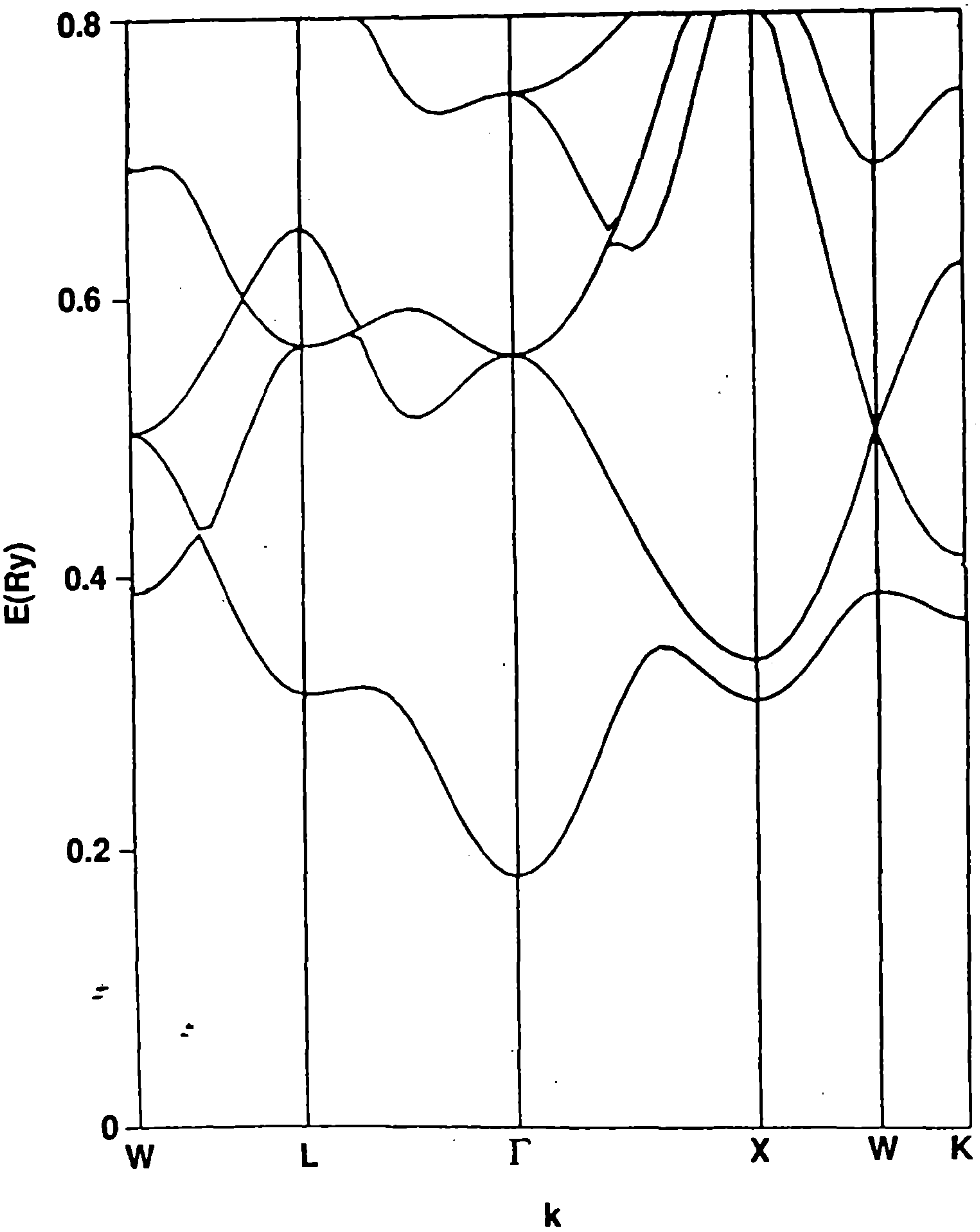
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0.2
0
E(Ry)
W
L
Γ
X
W
K
k